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Treatment of Metal Finishing Wastes by Use of Ferrous Sulfide

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TREATMENT OF METAL FINISHING WASTES BY USE OF FERROUS SULFIDE

by

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for

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16. ABSTRACT This demonstration was performed to study the operation, performance and economics of a new sulfide precipitation process ("Sulfex"TN), for treating metal finishing wastewaters. The study was performed by Holley Carburetor Division of Colt Industries, with assistance from the Permutit Company, at the carburetor manufacturing plant in Paris, Tennessee. Here "Udylite" processes are used for chromate conversion coatings on aluminum and zinc parts before assembly.

A newly installed Sulfex^{TN} system removes chromium and zinc from the plant's metal finishing wastewater. It also removes suspended material such as precipitated aluminum, iron and phosphates. Major steps in the system are: equalization and neutralization of untreated wastewater, precipitation of metals and sedimentation of suspended solids, polishing of settler effluent with dual media filtration, and final dewatering of settled sludge.

Results show all metals and suspended solids were removed to levels well below both the city sewer system limitations and the state guidelines. Excellent sludge dewatering resulted in the filter press without use of additional conditioning agents. No hydrogen sulfide odor was detected from the reaction process, treated effluent, or the solid waste produced. Jar tests were used for controlling effective wastewater treatment and economical operation.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a product of the above efforts. These studies were undertaken to demonstrate the practicability, effectiveness, and economics of a new heavy metal removal process using ferrous sulfide for heavy metal precipitation. The program was conducted on a hexavalent chromium and zinc bearing wastewater from a carburetor manufacturing plant. This waste is typical of discharges from manufacture of automative and bicycle parts, home appliances, electronic equipment, office machines, tools, wire, fasteners, etc. Therefore, technical data derived from testing at this plant is applicable to treatment of many other wastewaters in the metal finishing industry.

Such information will be of value both to EPA's regulatory program (Effluent Guidelines Division) and to the industry itself in arriving at meaningful and achievable discharge levels. Within EPA's R&D program, the information will be used as part of the continuing program to develop and evaluate improved and less costly technology to minimize industrial waste discharges. Besides its direct application to effluents from metal finishing industry, this technology may find application to treat metal-containing wastes generated by a host of other industries.

For further information concerning this subject, the Energy Pollution Control Division should be contacted.

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ABSTRACT

This demonstration was performed to verify the operational practicability and performance quality of a new sulfide precipitation process ("Sulfex"^{TN}), for removal of heavy metals from metal finishing wastewaters. Also, operational data was gathered for an economic evaluation of this process.

The study was performed by Holley Carburetor Division of Colt Industries, with assistance from the Permutit Company, at the carburetor manufacturing plant in Paris, Tennessee. Here, "Udylite" processes are used for chromate conversion coatings on aluminum and zinc carburetor castings before assembly.

A newly installed Sulfex^{TN} system removes chromium and zinc from the plant's combined metal finishing process wastewater. In addition, it removes suspended material such as precipitated aluminum, iron and phosphates. Major steps in the system are: equalization and neutralization of untreated wastewater, precipitation of metals and sedimentation of suspended solids, polishing of settler effluent with dual media filtration, and final dewatering of settled sludge.

Results show all metals and suspended solids were removed to levels well below both the City of Paris sewer system limitations and the State of Tennessee guidelines for indirect discharges to sewer systems. A dewatered sludge was produced as a firm, dry cake in a filter press without use of conditioning agents. No hydrogen sulfide odor was detected from the reaction process, treated effluent, or the solid waste produced. Jar tests were demonstrated to be a valuable tool for maintaining good process control and economical operation.

The chemical cost of "Sulfex"^{TN} has been found to be directly dependent upon the concentrations of combined zinc and hexavalent chromium present during the sulfide reaction process. "Sulfex"^{TN} was shown to be an economical as well as effective treatment process for this type of wastewater.

This report was submitted in fulfillment of Grant No. S-804648 by Holley Carburetor Division of Colt Industries under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 11, 1978 to August 11, 1978, and work was completed as of August 25, 1978.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

cu.ft.	-- cubic feet
ft	-- feet
ft^3	-- cubic feet
gal.	-- U.S. gallon
gpm	-- U.S. gallons per minute
hexchrome	-- hexavalent chromium
in	-- inch
kg	-- kilogram
kP_a	-- kilopascal (1 newton/m^2) = 6.895 psig
ℓ	-- liter
m^3	-- cubic meters
m/hr	-- meters per hour
m^3/hr	-- cubic meters per hour
mg/l	-- milligrams per liter
ml	-- milliliter
psig	-- pounds per square inch, gauge
scfm	-- standard cubic feet per minute
STP	-- sewage treatment plant
TSS	-- total suspended solids

SYMBOLS

Cr	-- chromium
Cr^{+6}	-- hexavalent chromium
Cu	-- copper
Fe	-- iron
FeS	-- ferrous (iron) sulfide
Zn	-- zinc

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SECTION I

INTRODUCTION

In April 1974, a laboratory and pilot plant study of a new wastewater treatment process, using sulfide precipitation, was sponsored by the Metal Finisher's Foundation under Grant No. R802924-01 from the Environmental Protection Agency. In July 1978, another study was undertaken to demonstrate effectiveness, operability, and cost of this new process called "Sulfex"^{TN} as a full scale installation at Holley Carburetor Company in Paris, Tennessee.

LABORATORY AND PILOT PLANT STUDY

This work is described in the report "Treatment of Metal Finishing Wastes by Sulfide Precipitation" EPA-600/2-7-049, February 1977*. The project involved precipitating heavy metals normally present in metal finishing wastewaters by a novel process which employs ferrous sulfide addition (Sulfex^{TN}) as well as by conventional treatment using calcium hydroxide for comparison purposes. A simulated metal finishing wastewater containing common heavy metals and chelating agents was used in this laboratory and pilot plant study. Sulfex^{TN} was demonstrated to be a technically viable process that is superior to conventional hydroxide precipitation for removal of copper, cadmium, nickel, chromium, and zinc from the given influent.

FULL SCALE STUDY

The present study was made during the start-up of a 7.9 m^3/hr (35 gpm) wastewater treatment system at the Holley Carburetor plant. Here, the manufacture of carburetors produces wastewater from chromate conversion coating of zinc and aluminum castings by a "Udylite" process. Combined wastewaters from these metal finishing operations contain heavy metal pollutant concentrations in excess of local and state limits set for direct discharge to the city sewer system. Therefore, a safe, reliable, and economic wastewater treatment process was needed by Holley to meet the imposed discharge requirements.

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*Schlauch, R. M. and A. C. Epstein, Treatment of Metal Finishing Wastes by Sulfide Precipitation, EPA-600/2-77-049, Environmental Protection Technology Series, Industrial Environmental Research Lab, Cincinnati, Ohio, Feb. 1977, pp. 1-74.

The metal finishing operations used at Holley involved degreasing, deburring, deoxidizing, acid etching, and chromate bath treatment to give carburetor castings corrosion resistant coatings. In the process, various materials including zinc, hexavalent chromium, aluminum, ortho- and polyphosphates, silicates, organic surfactants and chelants, as well as chelated metals, are released into the plant's wastewater discharge.

Since manufacturing specifications vary, all castings do not undergo treatment by each of these finishing operations. Furthermore, the production schedule is quite variable. As a result, the composition of the wastewater fluctuates periodically on hourly, daily and weekly bases.

This type of metal finishing operation is generally used for providing corrosion resistant coatings on surfaces of a wide variety of metal parts, components and appliances. Consequently, these wastewater characteristics are typical of many industrial manufacturing discharges that have to be treated to meet present and future discharge standards.

The laboratory and pilot plant study had demonstrated the effectiveness of Sulfex on a synthetically prepared metal finishing wastewater. The full scale system study at Holley is useful in further proving that the process is practical under actual manufacturing plant conditions. For example, Table 7 summarizes the overall effectiveness of the process in removal of pollutants. Figure 40 shows the average chemical operating cost, on a per shift basis. Other variables and economics are described individually on per shift and per year bases. Therefore, this study shows how practical, controllable, and economic it is to operate the process under the fluctuating contaminant loadings that are characteristic of many metal finishing wastewaters.

SECTION 2

CONCLUSIONS

EFFECTIVENESS

The effectiveness of the sulfide precipitation process, "Sulfex"^{TN}, has demonstrated that heavy metals can be removed from metal finishing wastewaters to very low levels. The effluent quality produced by this wastewater treatment process (as monitored by direct flame atomic absorption and diphenyl carbazide colorimetric methods for metal analyses) reveals that the process achieves metal values close to or less than are routinely detected by the accepted analytical methods (i.e. Cr and Fe detected at 0.05 mg/l, Cu and Zn detected at 0.01 mg/l).

ECONOMICS

The chemical cost of the "Sulfex"^{TN} process is directly dependent upon the influent metal loading of various heavy metals. At the Holley Carburetor plant, influent zinc and hexavalent chromium are the metal concentrations that dictate the dosage of ferrous sulfide that is required. Here, the chemical cost of "Sulfex"^{TN} is competitive with the cost of conventional bisulfite and hydroxide treatment for removal of average concentrations of zinc and hexavalent chromium in the untreated wastewater (i.e. about 34 mg/l Zn and 34 mg/l Cr^{+6}). Under these conditions, optimum "Sulfex"^{TN} costs range between $15.70 and $17.45 per eight-hour shift for combined zinc and hexavalent chromium. Separate removal costs for Cr^{+6} and Zn can not be accurately determined for this wastewater. On the other hand, the optimum conventional treatment cost of this wastewater is estimated at about $6.00 to $6.50 per kilogram of hexavalent chromium. Separate hydroxide precipitation of the zinc is estimated at $0.37 per shift. Therefore, conventional chemical cost for combined treatment of Cr^{+6} and Zn is estimated at $11.07 per shift for this wastewater.

When hexavalent chromium is present in combination with other heavy metals, as it is at Holley, there can be a savings in equipment cost with Sulfex^{TN} since the metals can be removed simultaneously in one step. But, as the concentration of zinc (or other heavy metals increases), the chemical cost of direct treatment by Sulfex^{TN} becomes increasingly more than by hydroxide precipitation. At Holley, the chemical cost for Sulfex^{TN} treatment is justified since conventional treatment can not effectively meet the city sewer limitations (i.e. 0.1 mg/l zinc maximum).

In all cases, however, the relative economics can be evaluated beforehand by the average heavy metal concentrations present in the wastewater. In some cases, it may be more economical to remove the bulk of the heavy metals by hydroxide precipitation, and apply Sulfex^{TN} as a polishing step when stringent criteria must be met.

Most of the basic equipment used for the Sulfex^{TN} process is the same as would be required for a conventional wastewater treatment process. Therefore, major capital costs as well as the operating costs are estimated to be commensurate for both of these treatment processes.

OPERATION

The operation of the wastewater treatment system at Holley is basically simple. Good control is maintained because the system is designed to handle sudden changes in wastewater flow and composition.

An equalization tank is an essential part of the system for dampening fluctuations in wastewater flow and metal concentrations into the reactor-settler unit. The concentrated waste sump receives spent metal finishing baths and slowly feeds them into the equalization tank. This sump is essential to minimize variations that could complicate the operation and downgrade the effectiveness of the waste treatment process.

Since it is possible some residual suspended solids carryover can occur periodically from the settler, the dual media filter is necessary to insure removal of suspended metals from the effluent before discharge to the city sewer system.

Without further use of coagulants or conditioners, a filter press will provide excellent dewatering of the settler sludge. A dry sludge cake is produced that releases easily from the press and is ready for disposal.

CONTROL

The pH control of the neutralization process is accomplished in the equalization tank. This type of system is satisfactory for maintaining an appropriate pH for effective metal precipitation in the reactor-settler unit. High concentrations of hexavalent chromium in the wastewater can cause moderate pH increases in the reactor-settler effluent. Controlling the pH at 8.0 in the neutralization step is an effective way of compensating for this pH increase.

Periodic visual jar tests performed on the reactor-settler influent are a satisfactory means of monitoring and controlling optimal ferrous sulfide and polyelectrolyte dosages. These visual tests, for determining chemical dosage requirements, eliminate the need for laboratory analysis of influent heavy metals.

OPERATING PERSONNEL

The need for wastewater treatment system operators must be determined on the basis of each plant. Due to frequent variation in the mode of the metal finishing operations at Holly, a full-time operator is required on each shift to monitor the wastewater treatment system. However, in installations where manufacturing processes are not as variable on a daily and weekly basis, a full-time operator may not be required on each shift.

In summary, it is concluded that Sulfex^{TN} is a more effective process than conventional wastewater treatment for complying with the stringent regulations pertaining to metal finishing wastes. The economics of each of these processes should be evaluated before deciding upon which type of process to use. Usually, the chemical operating cost, based on the presence and concentrations of various heavy metals, will be the parameter determining whether Sulfex is more practical as a direct application or as a polishing step.

SECTION 3

RECOMMENDATION

The "Sulfex"^{TN} process has demonstrated that more complete metal removal can be obtained and acceptable effluent quality achieved, compared to conventional hydroxide treatment of metal finishing wastewaters. But, the cost of precipitating most heavy metals (except hexavalent chromium) is higher by sulfide methods than by the hydroxide methods on a per unit weight of metal removed basis.

Study of present day technology reveals that hydroxide precipitation removes high percentages of zinc and other metals from metal finishing wastewaters. However, this removal method can still allow unacceptably high residuals of heavy metals in the treated effluent for discharge.

Therefore, in cases of very high metal loadings, a combination of the two methods in series should prove to be an economically attractive way of achieving superior quality effluents. In view of this, Sulfex^{TN}, as a polishing step following conventional hydroxide precipitation, is recommended when either heavy metal loadings on new systems are high enough to warrant the additional equipment or a conventional treatment system already exists.

SECTION 4

OPERATIONAL DESCRIPTIONS AND REQUIREMENTS

WASTEWATER CHARACTERISTICS FROM UDYLITE PROCESS AT HOLLEY

Type of Metal Finishing Operations

The arrangement of the equipment used to treat the castings by the Udylite process is flexible so that at any time, different castings can be treated by different specific processes as required by the customer. Basically, there are four processes commonly used. They are as follows:

Deoxidizing and zinc chromate conversion coating

Deoxidizing of zinc parts only

Chromate conversion of zinc parts only

Aluminum chromate conversion

These metal finishing processes utilize basically 15 tanks in coating carburetor castings. The castings are normally stacked on a rack, which is moved by a mechanical device in a specific manner. This is done so that the castings, depending upon the specific treatment required, can be dipped in selected process tanks for a predetermined duration. After each process treatment, the castings are countercurrently rinsed. City water is used in making the process solutions and for rinse water.

The Udylite process flow diagram is shown in Figure 1.

Sequence of Operations

Tank 1 - contains an alkaline cleaner to remove residual oils and coolants present on the surface of the castings. All zinc castings go through tank 1, whereas aluminum castings do not, because of alkaline attack on the aluminum. The chemicals present in this tank are: sodium carbonate, sodium hydroxide, silicates, organic chelating agents, and dissolved zinc.

Tank 2 - contains city rinse water

Tank 3 - contains city rinse water which is replenished continuously with fresh water and discharged through tank 2 to the waste discharge I.

Tank 4 - contains mild phosphoric acid, which functions as a deoxidizer and surface etch in removing zinc oxide from the surface of the zinc castings. A nonionic surface active agent is also present in the bath. The zinc oxide is formed on the surface by the process known as "thermal deburring" where zinc castings are exposed to an ignition of oxygen and hydrogen at a temperature of approximately 3350°C (6000°F). All thermally deburred zinc castings go through a deoxidizing cycle.

Tank 5 - contains city rinse water to remove residual phosphoric acid solution from the castings. Fresh rinse water is continuously replenished and discharged to the waste stream. This waste contains zinc and phosphates and is discharged to waste discharge II.

Tank 6 - not in use.

Tank 7 - not in use.

Tank 8 - contains concentrated chromate solution. Chromate conversion coating of aluminum castings is performed in this tank, if required by customer specifications. The zinc castings do not go through this tank. The chemicals contained in this tank are: chromates, fluorides and accelerators (proprietary agents for increasing the rate of coating formation). These accelerators are usually low concentrations of soluble metal salts.

Tank 9 - contains city rinse water. The fresh rinse water is replenished continuously and the waste containing chrome is discharged to waste discharge III.

Tank 10 - contains an acidic solution. All zinc castings, after they are cleansed with alkaline solution and rinsed, are passed through this tank. Any residual alkalinity left after previous rinsing is neutralized. The chemical composition of this bath includes: acid phosphate salts, glycol ether, anionic surface active agents, nonionic surface active agents and sodium chlorate.

Tank 11 - contains city rinse water. In this tank, excess acid is rinsed. The rinse water is discharged to waste discharge IV.

Tank 12 - contains a chemical deburring bath, mainly chromic acid. In this tank, zinc castings are chromated. The zinc castings may, or may not, be thermally deburred. The chemical composition of this bath consists of: chromic acid, sulfuric acid, acetic acid, and hydrochloric acid.

Tank 13 - contains city rinse water.

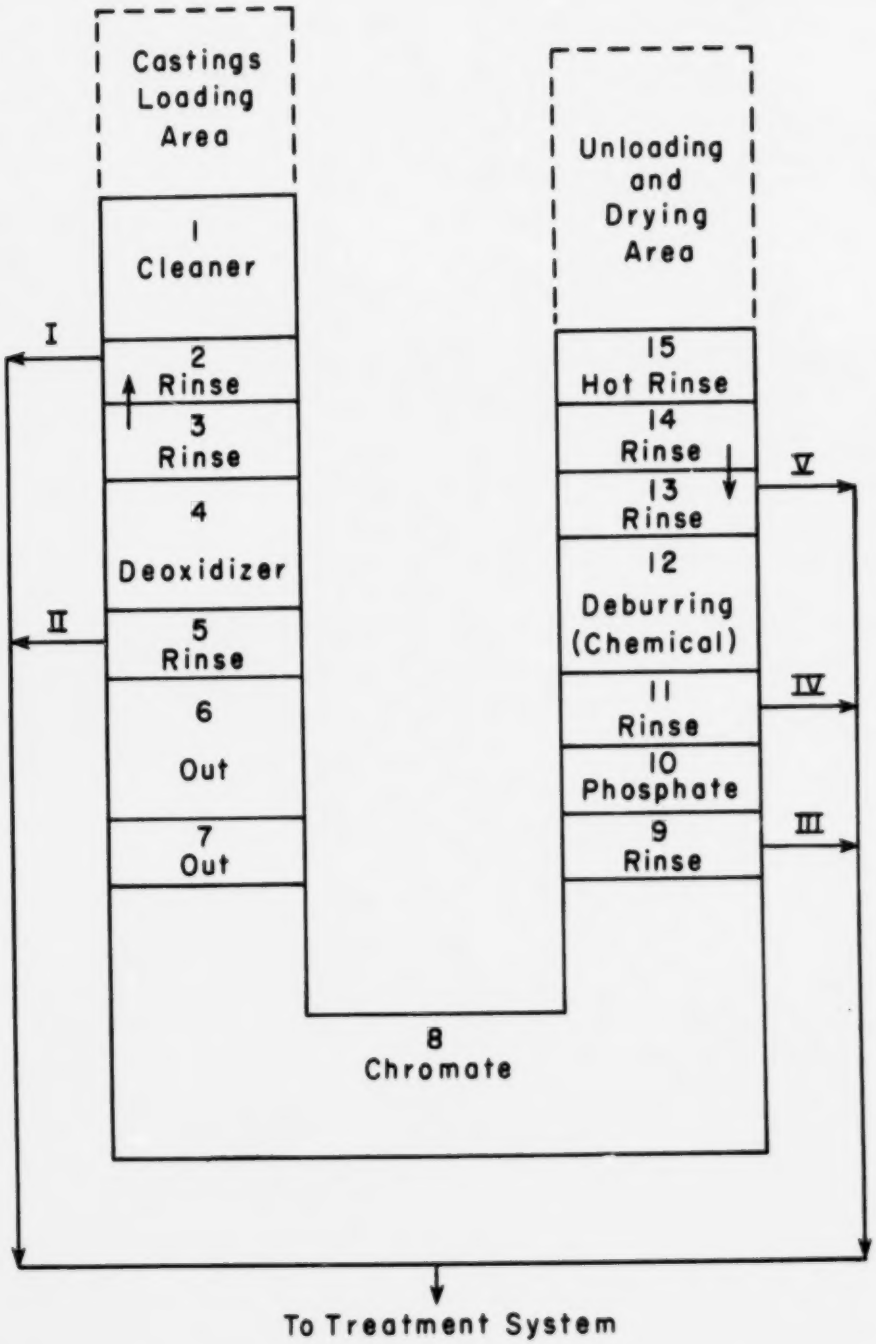

Figure I. Arrangement of chemical baths used in metal finishing processes at Holley Carburetor.

Tank 14 - contains city rinse water. The fresh rinse water is continuously replenished and is discharged through tank 13. The excess rinse water containing chrome is discharged to waste discharge V.

Tank 15 - contains city rinse water. In this tank, the castings receive a final rinse in water maintained at 140°F. This is done to raise the temperature of the casting to reduce the drying time. The castings are dried with hot air, after which they are transported to other areas for assembly.

Major factors affecting the composition of the wastewater discharge include production schedule, process selection and operational variations within each process.

The production schedule affects the amounts of each contaminant in the wastewater because the number and geometry of the castings being treated vary periodically. Therefore, chemical bath "drag out" varies with the contour and area of the total metal surface.

Selection of the finishing processes used determines which chemical solutions add drag out to the wastewater. A change in the number or combination of these processes in use varies the constituents in the wastewater.

Operational variations in specific processes are necessary because of high drag out conditions from, and deposition of materials into, the chemical baths. In order to maintain proper chemical concentrations in the process baths, fresh chemicals are periodically replenished and the non-effective concentrated chemicals are discharged into the wastewater system. Therefore, dissolved metal and precipitate concentrations tend to fluctuate significantly in the wastewater discharge.

Even without the influence of the partial discharges of process baths, the wastewater composition varies due to periodic build-up of precipitates in the rinse tanks and fluctuations in rinsewater flow rate. The rinse water pH tends to fluctuate between the pH values of 5.5 and 6.5. When portions of the acidic process baths are discharged, resulting wastewater pH may fall below 5.0. The solubilities of heavy metals in the wastewater stream are affected by these variable pH values as well as the variable concentrations of chelating agents and ionic species from the process and rinse tanks.

REQUIRED REMOVAL OF WASTEWATER POLLUTANTS AT HOLLEY

State Guidelines

The pretreatment program of the office of the State of Tennessee at Nashville provided information on the Tennessee guidelines for the waste discharge to the municipal treatment plant.

The State of Tennessee has established guidelines and criteria for indirect discharges, including metal finishing wastes discharged to sewage treatment systems. These guidelines listed in Table 1 are based on available technology, reflecting Best Practical Treatment (BPT). Portions of these guidelines were derived from the proposed BPT pretreatment standards for the electroplating industry. These values are considered as optional guidelines, since they are achievable by available technology, but are not necessarily limiting for protection of sewer treatment systems.

TABLE 1. STATE OF TENNESSEE GUIDELINES FOR INDIRECT DISCHARGES TO SEWER SYSTEMS

Parameter	Maximum concentration, mg/l
Zinc	5.0
Hexavalent chromium	0.05
Total chromium	5.0
Copper	5.0
Total suspended solids	1,500 if there is a problem involving combined sewer
Petroleum, mineral oil, vegetable and animal oil	100

City Requirements

The City of Paris, Tennessee passed an ordinance on July 6, 1978 establishing the limiting concentrations in waste as received at the city sewer treatment system, based on the protection criteria, pass through, sludge concentation, and unit operation inhibition. These limits are listed in Table 2. These values are considered as mandatory guidelines since they are based on actual toxicity levels that have been documented.

TABLE 2. LIMITING CONCENTRATIONS IN THE WASTE RECEIVED AT CITY OF PARIS SEWER TREATMENT SYSTEM

Parameter	Maximum concentration, mg/l
Boron	0.2
Cadmium	BDL*
Chromium (hexavalent)	0.4
Chromium (total)	1.0
Copper	1.0
Cyanide	0.2
Lead	BDL*
Nickel	0.1
Zinc	0.1

*Below Detectable Levels

The second basic guuideline, set forth in a City of Paris ordinance, pertains to protection criteria for the sewage treatment plant. It contains an added factor of safety to ensure that the inhibition level in the influent to the sewage treatment plant is never equalled or exceeded. These protection criteria are listed in Table 3. As is indicated by the range values listed for each pollutant, the recommended discharge concentration for a specific point source depends on its volume with respect to that of the sewer treatment plant.

TABLE 3. CITY OF PARIS PROTECTION CRITERIA FOR SEWAGE TREATMENT PLANTS

Parameter	Recommended concentration, mg/l
Zinc	0.04-5.0 depending on STP
Hexavalent chromium	0.5-5.0 depending on STP
Copper	0.5
Total suspended solids	Depending on STP design capacity
Petroleum, mineral, vegetable, and animal oils	Depending on STP design capacity

Reference - EPA Document 430-9-76-0172, Federal guidelines, State, and local pretreatment program, January 1977.

As mentioned earlier, the waste treatment equipment employing the "Sulfex"^{TN} process was provided to treat one specific waste discharge, Holley Carburetor's metal finishing waste. The metal finishing waste represents approximately 20 volume percent of the total Holley facility flow discharged to the city sewer system. Obviously, if the parameter concentrations in the discharge from the "Sulfex"^{TN} treatment system are equal to or below the protection criteria of the sewage treatment plant (Table 3), there can be no possibility of exceeding the defined inhibition concentrations at the sewage treatment plant, provided all the other contributing discharges are not contaminated. Therefore, this report is written with major emphasis on determining the effectiveness of the "Sulfex"^{TN} process in treating Holley's metal finishing discharge to meet the most stringent State and City protection criteria for all listed pollutants.

DESCRIPTION OF WASTEWATER TREATMENT SYSTEM AT HOLLEY

The basic components of the wastewater treatment system are: wastewater collection sumps, two-stage equalization-neutralization tanks, reactor-settler (i.e. "Precipitator")*, and dual media polishing filter. Sludge dewatering is handled by a collection sump and filter press. A flow diagram of this waste treatment system, including material balance, is shown in Figure 2.

The wastewater flow from each compartment of the Udylite plating equipment flows to a common trough. From this trough, the combined flow is directed to a small sump, approximately 0.37 m^3 (100 gallons) in capacity. A float controlled sump pump lifts the raw wastewater to the first stage neutralization tank of the waste treatment system. This tank is used to help equalize the flow and to adjust the pH of the waste, with lime, to the 6.5-7.2 range. The wastewater from the first stage flows by gravity into a separate second stage where lime is used for the final pH adjustment. The set point for pH in the second stage is 8.5 with recycle conditions occurring at pH values 8.0 and 9.0. The pH adjusted wastewater is then pumped to the Precipitator.

In the Precipitator, the wastewater is allowed to contact freshly prepared ferrous sulfide and a suitable polyelectrolyte. Dissolved metals react with the ferrous sulfide to form an insoluble, stable precipitate. A sludge blanket is maintained in the Precipitator to insure that there is enough solids contact to promote precipitation and coagulation of dissolved metals and suspended material. The treated water is pumped from the Precipitator to a dual media filter for additional removal of suspended solids.

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*The term "Precipitator", used throughout this report, refers to a proprietary upflow, solids contact reactor-settler unit, manufactured by The Permutit Company, Inc., Paramus, New Jersey.

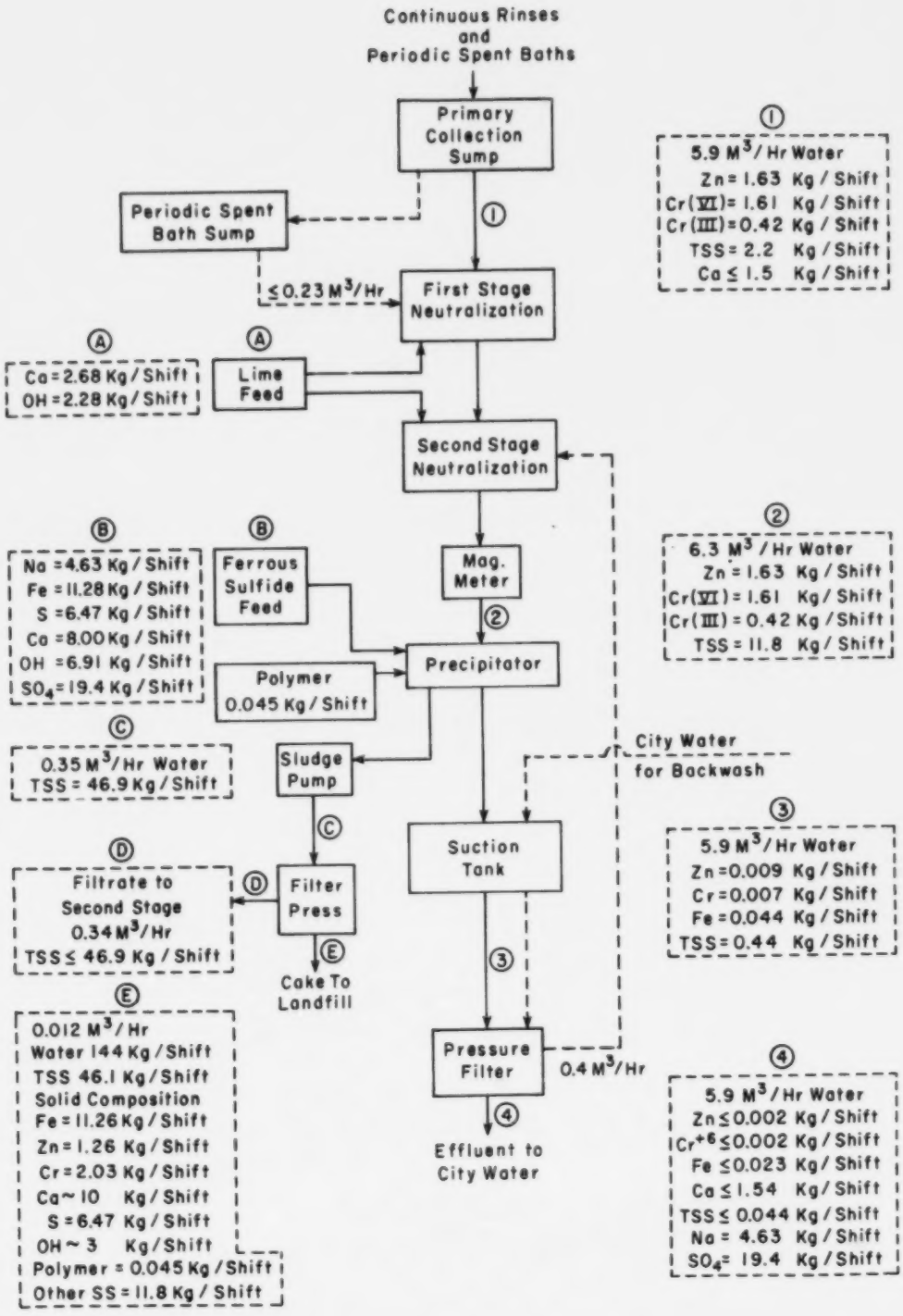

Figure 2. Sulfex™ system flow plan and material balance at Holley.

The blowoff (periodic underflow) of concentrated sludge from the Precipitator (composed of metal hydroxides, phosphates, and heavy metal sulfides, etc.) flows, by gravity, to a sludge sump for dewatering. The sludge from the sump is pumped to a filter press which then concentrates the blowoff to the consistency of a dry cake.

DESCRIPTION OF SULFEX^{TN} PROCESS OPERATION

Neutralization Process

For optimum performance of the "Sulfex"^{TN} process, the pH of the wastewater should be maintained within the 8.0 to 9.0 range. This is accomplished at Holley Carburetor by use of a two-stage pH adjustment system. Since the equalized water is always acidic, only lime is provided to adjust pH.

The first stage of this two-stage system consists of a well-mixed holding tank, a pH sensor, and a lime pump for pH adjustment. Mixing is provided by a high-speed mixer. At the designed flow of 8.4 m^3/hr (37 gpm), the average retention time in this tank is 1.65 hours.

Lime is fed to the first stage tank by a diaphragm metering pump. The pump is activated by a signal from the pH electrode in the tank. The set points for pH in this stage are 6.5-7.2. When pH adjustment is required in this first stage, the lime pump starts only at pH 6.5, and continues to pump until the pH is at the high limit of 7.2. By the use of this system, the pH in the first stage normally varies between 6.5 and 7.2. If a highly acidic waste is introduced to the system, the pH in this stage might go below this range.

The waste from Stage #1 overflows directly into the second stage tank of the neutralization system. The second stage utilizes a proportional pH controller and includes a large, well-mixed holding tank, pH sensor, high and low level alarms, an internal recycle system, and transfer pumps to the Precipitator.

The holding tank, in addition to providing stable pH correction, serves to equalize concentration fluctuations of influent metals. Mixing in this stage is again provided by a high speed mixer. A secondary function of the pH recorder/controller (in this stage) is to activate low pH recycle and alarms and control the lime feed pump.

The lime feed pump to this stage is an electronically controlled stroke diaphragm metering pump. The stroke of this pump is automatically controlled in accordance with the deviation of pH from the set point. The set point for pH in this stage is 8.5 with the low and high pH recycle conditions set at values of 8.0 and 9.0, respectively. During the recycle condition, the flow is recycled within the tank until pH is again within the desired range. To accommodate inlet flow while in recycle, this stage is designed to run with the tank partially full during normal conditions.

At low liquid level, the system also goes into recycle. The low liquid level recycling condition occurs 0.62 meters (2 ft.) from the bottom of the tank. A high level alarm is provided to alert the operator that he should increase the rate of withdrawal of waste from the second stage.

The pH adjusted waste is pumped from the second stage of the neutralization system to the Precipitator. Since it is important to maintain flow out of the second stage, a spare pump is provided. During this test program, the operation of each pump was alternated daily.

Process Controls

The control panel at Holley Carburetor contains various switches, level alarms, pH recorders, a pH controller, and an automatic control system for chemical feeds.

The pumps and agitators are activated by various switches located on the control panel. All the switches operate in one of three modes; hand, off, or automatic.

Included in the control panel is the automatic pH control system. As has already been explained, the first stage pH control allows the pH to vary between 6.5-7.2, while the second stage pH varies between 8.0-9.0.

Prepared concentrations of ferrous sulfide slurry and polyelectrolyte solution are metered from individual feed tanks (8 to 48-hour supplies) to achieve the required concentration of chemical agents into the Precipitator influent. The chemical feed systems, both polymer and ferrous sulfide, are controlled by the magnetic flow meter. Both chemicals are fed proportionally to wastewater flow to the Precipitator. The feed systems are activated by a counter which responds to pulses from the flow meter. Each pulse represents a metered volume of wastewater flow. When a preselected volume has passed, the chemical feed system is activated. The feed system continues to deliver chemical until a preset timer times out. The process keeps repeating so that over a period of time the correct dosage of each chemical is delivered to the Precipitator.

Level switches activate a horn and a light, so that the operator is alerted when a feed supply tank is running low.

Precipitator Operation

The rectangular solids contact settling device "Precipitator" is used to remove most of the pollutant metals from Holley's waste stream.

Functional Aspects--

The function of the Precipitator is to bring about two basic processes of wastewater treatment. One process is chemical (reduction and precipitation) and the other is physical hydraulics (separation of the solid particles from the liquid).

To enhance the chemical process, the solution phase (wastewater) and the solid phase (precipitated particles) are brought into intimate contact through proper control of the hydraulic processes. This means a fluidized suspension of solids is maintained in the solution phase which serves to minimize chemical reagent usage. Therefore, the effectiveness of the chemical reaction process is inherently dependent upon proper design and control of the hydraulics.

In the "Sulfex"^{TN} process, the proper control of chemical and physical processes is accomplished by adding ferrous sulfide to the wastewater stream entering the top of the Precipitator mixing zone (Zone A, Figure 3). Ferrous sulfide and liquid waste then intermix on their way through the mixing zone. The chemical reactions are carried out during this mixing process and growth of precipitated particles is induced.

Following the chemical reaction and particle growth stage, the liquid-solid suspension flows into and up through the settling zone (Zone B, Figure 3). In this zone, the upflow velocity diminishes continuously so that the precipitated particles settle out while the treated liquid flows upward and out through the effluent collection system. Since the liquid velocity continually decreases, and the solid particles vary in their settling rates, differentiated layers of settling particles within this zone establish a dense blanket of fluidized solids.

This "sludge blanket" has a dual function. It acts as a reservoir for storing excess ferrous sulfide that is available for reaction with residual dissolved heavy metal. Some of these concentrated fluidized solids work their way back into the mixing zone (due to flow patterns and concentration differences) where they establish an excess of reactive sulfide for enhancement of the chemical process. The secondary function of the settling zone blanket is to filter out or trap unsettleable and colloidal particles that may pass through the mixing zone.

Start-up--

For start-up purposes, the concentration of ferrous sulfide needed is determined by calculation of stoichiometric requirements for the average heavy metal concentrations analyzed in the plant's wastewater discharge. The feed rate of ferrous sulfide is then adjusted to 3 to 5 times the calculated stoichiometric requirement until a sludge blanket develops. This normally takes one to three days depending on the metal concentration in the wastewater and the average flow rate to the Precipitator.

Normal Operation--

After start-up, jar tests are used to periodically determine the required ferrous sulfide dosage. In the jar tests, the disappearance of the characteristic yellow chromium color is noted for various ferrous sulfide dosages applied. If no hexavalent chromium exists in the untreated wastewater, the jar tests can be modified to show the residual activity of the fluidized blanket in the mixing zone. To do this, a standard chromate solution is applied at various concentrations to samples of the fluidized blanket existing in the mixing zone.

The concentration of reactive ferrous sulfide existing in the blanket samples will be detected by the concentration of standard chromate reduced. The concentration of active ferrous sulfide in the mixing zone is normally maintained at a level sufficient to treat approximately two or three times the average heavy metal loading. The applied ferrous sulfide dosage to the Precipitator can be regulated to achieve this level of blanket activity.

These jar tests, performed once or twice per 8-hour shift, are sufficient to determine ferrous sulfide dosages for optimum operation. Therefore, it is not necessary to perform metal analyses on the untreated wastewater on a routine basis to determine the ferrous sulfide requirement.

To facilitate particle growth and settling properties, a polyelectrolyte is introduced into the mixing zone of the Precipitator. The polymer flocculates the suspended solids in this turbulent flow region before the fluidized mass flows into the settling zone. As the particles are stirred, they become coarser. Small particles combine into larger masses aided by the action of the polyelectrolyte.

Once in the settling zone, the particles continue to grow until they can no longer be supported by the upward velocity. Then, they settle back into a region of higher velocity. In continuing to grow in size and density, the particles settle down through the settling zone until they are so heavy that they fall into either the concentrator zone (Zone C of Figure 3) or are drawn back into the mixing zone by a draft caused by the rotation of the agitator paddles. Migration of small particles out of the mixing zone is counterbalanced by the return of enlarged particles back in so that a concentrated blanket is also maintained in the mixing zone when equilibrium is attained.

Within the concentrator zone, there is normally very low or no liquid movement. The particles settle into a compressing mass of higher solids concentration. The concentration of solids in this zone is usually one to three percent by weight. During this study, it varied from 14,000 to 24,000 mg/l and averaged 16,800 mg/l as suspended solids.

In order to insure steady Precipitator operation, the concentrated solids are periodically removed by a "blowoff" operation. The blowoff is adjusted so that the top level of the settling zone blanket varies minimally with time.

Sampling points are located through the Precipitator. On Figure 3, they may be seen as points #1 through 5. Sample pipes extend from these points to a sink. At this sink, samples of the different zones may be taken. The regions sampled are: point #1 - upper mixing zone, point #2 - lower mixing zone, point #3 - lower settling zone, point #4 - upper settling zone, and lastly, point #5 - the effluent from the Precipitator. By obtaining samples from these regions, the effectiveness of the polymer dose, and the concentration of the sludge blanket, may be indicated. The observed profile of these regions on a volume percent solids* basis is as follows: point #1 - 25%, point #2 - 30%, point #3 - 42%, point #4 - 0% to 50%, and point #5 - 0%.

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*Volume percent solids are measured as the ratio of settled solids volume to total sample volume at 10 minutes of quiescent settling.

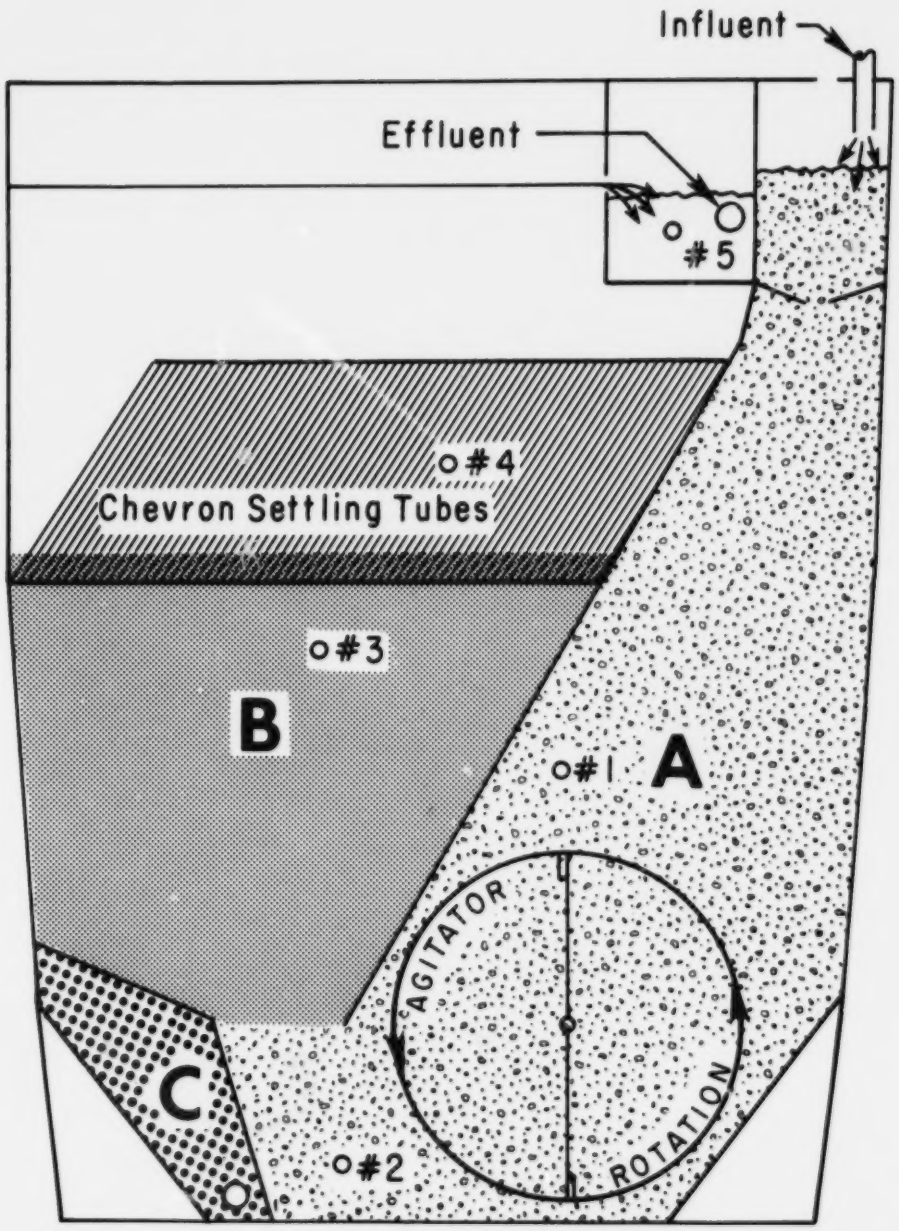

Figure 3. Cross-section of Precipitator mixing and settling zones.

Blowoff Operation--

The blowoff sludge from the Precipitator is composed of unreacted ferrous sulfide, other metal sulfides, hydroxides, phosphates, etc. amd is periodically withdrawn so that a steady-state sludge blanket can be maintained. The frequency of blowoff is automatically controlled in proportion to flow to the Precipitator. The duration of blowoff is chosen by the operator. It is desirable to have an interval of at least 10 to 15 minutes between blowoffs so that precipitated material has time to concentrate and settle in the concentrator section of the Precipitator.

Precipitator blowoff flows by gravity to a sludge pit. The pit has a high level alarm and float control recycle valve for filtrate return from a filter press.

The float control recycle valve comes into use when the level in the sump is 0.23 meters (9 inches) from the bottom of the sump. When the level in the sump reaches this point, the valve automatically opens and the filtrate from the filter press recycles back into the sump. This is to insure that the flow to the sludge pump is not interrupted.

From the pit, the sludge is then pumped to the filter press. A positive displacement sludge pump is used, capable of pumping in excess of 4.54 m^3/hr (20 gallons per minute) at zero KPa (zero psig) discharge pressure. A variable speed unit attached to the motor allows the selection of variable pumping rates. A pump discharge pressure gauge with a preset alarm contact signals that the filter press is full of sludge. At this point, it has to be manually emptied, requiring about 10 or 15 minutes of the operator's time to get back into service.

Chemical Feed System

A magnetic type flow meter is installed in the inlet to the Precipitator to control the ferrous sulfide and polyelectrolyte feed systems, and the Precipitator blowoff frequency. The ferrous sulfide and polyelectrolyte are fed proportionally to flow based on a signal from the flow meter.

The ferrous sulfide is fed to the system as a 2.2 percent weight per unit volume (i.e. 22 grams/liter) slurry. (The dosage used at Holley normally varied between 200 mg/l and 600 mg/l.) These required dosages are determined by the use of a visual jar test. When a change in dosage is indicated, timers are manually adjusted on the control panel accordingly.

The ferrous sulfide feed system consists of two separate tanks. Freshly prepared slurry is fed from only one tank at a time. A low level alarm is provided to alert the operator that it is time to switch to the next tank of ferrous sulfide. On the average, one tank of ferrous sulfide lasts from 8 to 12 hours for the wastewater loadings at this plant.

The ferrous sulfide slurry is prepared by adding hydrated lime, $Ca(OH)_2$; sodium sulfhydrate, NaHS; and ferrous sulfate, $FeSO_4$ to the ferrous sulfide tank. After the slurry is prepared, it is constantly stirred by a slow speed agitator.

The polymer used to flocculate the metal sulfides in the Precipitator is a cationic guar derivative which works well in the concentration range of 5 to 15 mg/l. The polymer solution strength is prepared at 0.5 percent weight per unit volume (i.e. 5 grams/liter) and is fed proportional to wastewater flow.

The contents of a polymer storage tank lasts for 40 to 50 hours depending on the flow to the system. Polymer is injected into a dilution water stream which is then distributed through a header into the mixing zone of the Precipitator. In this manner, the polymer disperses quickly and thoroughly.

Suction Tank and Dual Media Filter Operation

The Precipitator effluent flows by gravity into a suction tank. The suction tank insures an uninterrupted flow of water to the dual media pressure filter. The flow from the suction tank is pumped to the filter by means of a centrifugal pump. Two such pumps are provided. One pump is used during service; the two pumps are used jointly for filter backwash.

The dual media filter is installed with a bed that consists of 1.2-1.5 mm effective size anthracite on top of 0.55-0.65 mm effective size fine sand. The supporting bed is composed of coarse sand and fine and medium gravel.

The 1.22 m (4 ft.) diameter filter operates at 7.8 m/hr (3.18 gpm/ft^2). During normal operation, the filter receives an average influent of 5 to 10 mg/l of suspended solids and produces an average effluent of 1 mg/l or less suspended solids. The normal service time for this filter under Holley's operating conditions is 16 hours. The effluent from the filter is presently sent to the sewer but in the future, it may be reused as plant process water.

The end of service cycle, for a filter of this type, is normally determined by the pressure drop across the bed. At a flow of 6.8 m^3/hr (30 gpm) and service time of 16 hours, the maximum pressure drop observed at Holley was 34.5 kilopascal (5 psig).

For convenience, the filter is backwashed after plant operation is stopped for the day. As part of the backwash procedure, the filter is first air scoured at 61.1 std. m^3/hr (38 scfm) for 5 to 10 minutes and then backwashed with city water at 43 m^3/hr (188 gpm) for 10 minutes via the suction tank with float controlled make-up. The filter is then rinsed at 5.67 m^3/hr (25 gpm) for approximately 5 minutes. The backwash wastewater is returned to the second stage tank of the neutralization system for suspended solids removal in the Precipitator. A level alarm in the neutralization tank indicates whether or not there is sufficient room for backwash water.

Filter Press Dewatering

The equipment used to dewater the sludge at this installation is a filter press. This press is 0.46 m x 0.46 m (18 in. x 18 in.) and is capable of holding 0.147 m^3 (5.2 cu.ft.) of filter cake. The area available for filtration is 9.3 square meters (100 square feet), and the filter cloth is made of polypropylene.

For purpose of study, this unit was run in various modes of operation: constant pressure, constant pump rate, and constant flow rate. The feed concentration to the press was in the range of 14,000 to 24,000 mg/l of suspended solids.

The resultant mode of operation selected at Holley was that of constant pump drive speed. While operating in this manner, the press requires no supervision until the pressure gauge on the outlet of the pump signals a high pressure condition 344.8 kilospascal (approximately 50 psig). At this pressure, a good firm cake exists and the filtrate, returning to the second stage of the neutralization system, is still relatively low in suspended solids. This pressure is chosen because the resulting cake breaks cleanly from the cloth and the down time for emptying is minimal (10-15 minutes). At a higher pressure operation, more time is required to manually scrape the cake from the cloth.

SECTION 5

TEST PROGRAM AND PROCEDURES

MONITRORING PROCEDURES FOR OVERALL TREATMENT SYSTEM

It was initially established between Holley, the EPA, and Permutit that 28 days of operation was necessary to adequately demonstrate the effectiveness of the wastewater treatment process. The 28-day period was the anticipated minimum time it would take to have the different "worst condition" combinations of metal finishing processes represented in the wastewater. During the time of this study, the metal finishing operations were performed for two shifts (16 hours) per day for five days per week.

Sampling Procedures for Regulated Constituents

Start-up of the waste treatment system, training of two operators, sampling to demonstrate overall waste treatment process effectiveness, and monitoring of individual unit processes were carried out during the first four weeks of the test program. During this time, two Holley operating personnel assisted by Permutit technical personnel were alternating on the two shift per day, five-day per week waste treatment plant start-up and demonstration test. Sampling and monitoring were actually conducted for 22 days following a six-day mechanical start-up period.

The sampling, necessary to demonstrate that the wastewater treatment process effluent meets both the state guidelines and the city protection criteria, was a routine collection and analysis of the raw influent and final effluent. The raw wastewater was monitored by taking grab samples from the primary collection sump for the first two weeks, and then composited samples of this source for the remaining portion of the test. The final effluent was monitored by collecting both composite and grab samples for the first four weeks and composites only, after this time.

The raw influent grab samples were collected every two hours for one 8-hour shift per day during the first week. For the second week, influent grab samples were collected every four hours over two shifts daily. For the remaining portion of the demonstration test, only composite samples of the raw influent were collected for two shifts daily.

These composite raw influent samples were collected by running 1/4 inch diameter tubing from a sample valve on the primary collection sump pump discharge to a 15 gallon plastic tank. Whenever the sump pump discharged waste to the first stage neutralization tank, sample would be collected in

the 15 gallon tank. After each 8-hour shift, a volume of approximately 10 gallons of a composite sample was collected (depending on the flow of plant wastewater to the sump during that shift).

Final effluent grab samples were collected from the pressure filter outlet sample tap. These samples were taken at the approximate midpoint of each 8-hour shift for the first four weeks of the demonstration test.

In addition to the grab sample each shift, a final effluent composite sample of each shift was collected from an automatic sampler. This sampler is installed on the filter outlet line adjacent to the outlet sample tap. It consists of a solenoid valve that is controlled by volume of flow through the magnetic meter on the inlet to the Precipitator. The frequency of the flow volume counter for this sampler (i.e. frequency of the pulse that triggers the solenoid valve to open) was set so that at 5.9 m^3/hr (26 gpm) Precipitator rate, the sampler would open about every 15 minutes for about 10 seconds. At this setting, about 0.015 m^3 (4 gal.) of composite sample was collected per shift in a 20 liter (5 gal.) pail. The final effluent composites were collected during each shift for a 5-week period.

The samples collected from the raw waste and final effluent sources were analyzed by a local commercial laboratory for the following constituents:

(1) Total Chromium

(2) Hexavalent Chromium

(3) Zinc

(4) Copper

(5) Iron

(6) Total Suspended Solids

In addition, one grab sample per week of the final effluent was analyzed by the same laboratory for oil and grease concentration.

In order to provide sufficient sample volume, a 500 ml sample was collected for each hexavalent chromium analysis and a 500 ml sample for the other heavy metals collectively. A 3.8 liter (one gallon) sample was collected for each suspended solids analysis and 3.8 liters (one gallon) was collected for each oil and grease analysis. Hexavalent chromium samples were preserved by adding sulfuric acid solution to obtain pH less than 2.0. The samples for other metal analyses were preserved by addition of nitric acid solution to obtain a pH value less than 2.0. The oil and grease samples were preserved with sulfuric acid to pH less than 2.0 and suspended solids samples were left unpreserved.

Analytical Methods Used for Regulated Constituents

The analytical methods used were as follows:

(1) Total iron - ASTM Method D - 1068-77 - Method C

(2) Total zinc - ASTM Method D - 1691-77 - Method C

(3) Total copper - ASTM Method D - 1688-77 - Method D

(4) Total chromium - ASTM Method D - 1687-77 - Method D

(5) Hexavalent chromium - Standard Method - 14th Edition Method 307B

(6) Suspended solids - EPA STORET 00530

(7) Oil and Grease - EPA STORET 00556

Total chromium, iron, copper and zinc were analyzed by atomic absorption spectrophotometry. The diphenylcarbazide colorimetric method was used for hexavalent chromium. Suspended solids were analyzed by gravimetric procedures. The method used for oil and grease was separatory funnel extraction with freon.

MONITORING PROCEDURES FOR SEPARATE PROCESS STEPS

Samples were drawn during each shift for various analyses and measurements at different stages of the system. The samples were taken at regular time intervals to determine the degree of treatment being achieved in each step of the waste treatment process.

Monitoring of Chemical Feed Consumption

The consumption of treatment chemicals including ferrous sulfide slurry, polyelectrolyte, and lime was monitored by measuring the drawdown of chemical solutions or slurries from their holding tanks about every two hours. These rates were recorded on the log sheets. Adjustable stroke and rate setting on the chemical metering pumps allow the operators to change the rate of chemical drawdown.

Monitoring by Jar Tests

Jar tests were conducted at a rate of about two per shift to estimate the ferrous sulfide dosage requirement of the influent to the Precipitator. To perform these tests, a sufficient sample was drawn from the surface of the second stage neutralization compartment, which is a completely mixed tank. This sample was subdivided into one liter portions. Six of these portions were tested at a time by equally stirring them at rates simulating the mixing conditions in the Precipitator's mixing zone. Increasing dosages of ferrous sulfide (FeS) slurry were added to each sample during the stirring process. Polyelectrolyte was also added to increase the rate of flocculation of precipitated particles.

After 20 minutes of stirring the chemicals with the wastewater samples, the precipitated solids were permitted to settle for 5 to 10 minutes. The color of the supernatant was observed for disappearance of yellow hexavalent chromium color. In some of these jar tests, hexavalent chromium and zinc were measured with colorimetric spot test kits.

The dosages of ferrous sulfide required to produce a colorless supernatant liquid were used as estimates to guide the operators in setting the feed rate of slurry to the Precipitator. To aid the operator, a curve chart was plotted showing actual slurry tank drawdown rates corresponding to ferrous sulfide requirements indicated by the jar tests.

This method of monitoring was found acceptable for making necessary adjustments in ferrous sulfide feed to the Precipitator. Since the average turnover rate in the pH neutralization-equalization system is about 5.2 hours, fluctuations in wastewater metal concentrations, large enough to warrant chemical feed adjustments, were not found to occur more frequently than this time interval.

Monitoring of pH Value

The pH of the raw wastewater was measured with a portable pH meter and recorder about every two hours on log sheets. The pH of the first stage neutralization, controlled automatically, was read from a meter on the control panel. Also, the automatically controlled second stage pH was monitored by a recorder on the control panel. Both of these pH values were also recorded manually on the log sheets along with the raw waste pH. A fourth pH measurement was made on the Precipitator effluent with the portable pH meter and recorded on the log sheets with the others.

Sludge Blanket Settling Tests

For purpose of study, the concentrations of precipitated solids that make up the sludge blanket in the mixing and settling zones of the Precipitator were monitored every one to two hours. This sampling frequency is not necessary in normal operation of the Precipitator. But, these frequent tests were made to evaluate and document the concentration of sludge blanket that existed in various portions of the unit.

Four sample points are located on the Precipitator for withdrawing blanket samples from the different zones. The samples taken from each point are as follows:

Point No. 1 - Upper mixing zone

Point No. 2 - Lower mixing zone

Point No. 3 - Settling zone below chevron settling tubes

Point No. 4 - Settling zone inside of chevron tubes

A fifth tap samples the Precipitator effluent pocket, taking clarified liquid after it flows over the weir. Samples of 100 milliliter volume were drawn from each of these sample points and allowed to settle 10 minutes for observation. The volume of settled material with respect to initial sample volume is called the volume percent solids settled. These measurements were recorded on the log sheets to document the relative concentrations of settleable solids in different zones of the sludge blanket, with respect to each other and with time.

Observation of changes in these concentration profiles show the operator whether or not the sludge blanket is in a stable condition. Increases or decreases in sludge blanket height and concentration indicate to the operator whether the blowoff rate of concentrated sludge should be increased or decreased.

Suspended Solids Into and Out of Precipitator

The suspended solids loading to the Precipitator and to the dual media filter was checked daily during this demonstration test. This was accomplished by taking grab samples from the second stage neutralization tank (Precipitator influent) and the Precipitator effluent (pressure filter influent) for one shift per day. Normally, these grab samples were taken during the first shift between two and six hours after start-up. The samples were immediately filtered through 0.45 micrometer pore diameter membrane filters by vacuum. The membrane filter discs were then saved in Petri dishes and labeled as to source, time, date, and volume of sample filtered. These samples were later brought to the Permutit laboratory in Princeton, New Jersey for drying, weighing, and gravimetric analysis of the suspended material that was removed by the filtration.

In addition to these daily samples, taken for suspended solids measurements in the Precipitator influent and effluent, samples of sludge blanket points # 1, #2, #3, and #4 were taken several times a week for gravimetric suspended solids determination. These suspended solids concentrations, as mg/l, were then compared to the volume percent solids already recorded on the log sheets, for the sludge blanket samples.

The suspended solids concentrations thus obtained are only regarded as good estimates of the true values since each Millipore was not preweighed. In making these suspended solids determinations, the average weight of a membrane filter disc from each package was used. Due to the degree of filter weight variation, the suspended solids concentrations resulting in 10 mg/l and higher values are reasonably accurate, but those under 10 mg/l should be regarded only as estimates of the true values.

Total Heavy Metal Loadings Into and Out of Precipitator

To check the relative effectiveness of the Precipitator in removal of total heavy metal values, grab samples were collected from the second stage neutralization and the Precipitator effluent during this study. One grab sample was taken during each shift, from these locations, for analysis of heavy metals. Normally, these grab samples were taken at approximately the middle of each shift and correspond, on a point in time basis, to the grab samples taken from the final filtered effluent during the shift.

The metals analyzed in the Precipitator influent include total and hexavalent chromium as well as zinc, iron, and copper. Samples of the Precipitator effluent were not prepared for hexavalent chromium analysis since the filtered effluent was sampled at the same time and this source has the same hexavalent chromium concentration. Precipitator influent was analyzed for hexavalent chromium as well as the other heavy metals (i.e. total Cr, Zn, Cu, and Fe).

These samples of Precipitator influent and effluent were analyzed for metals at the Permutit R&D Center in Princeton, New Jersey. All samples were appropriately preserved and labeled for shipping to the laboratory for analysis. Proper preservation by acidification is important to insure the metals will not be adsorbed by the plastic containers during shipment and storage.

Whereas, all raw influent and final effluent samples were analyzed within 24 hours of collection, the Precipitator influent and effluent samples were approximately a week old before the analyses could be made. The one week period required for shipping and handling, however, has been shown to have no significant change on the original composition of the sample. This is plainly demonstrated by comparing analyses of duplicate samples run by two different laboratories. The local commercial laboratory analyzed the sample within 24 hours of collection, but the other laboratory (in New Jersey) analyzed the duplicate sample approximately one week later. Tables 4 and 5 show a list of the results obtained for identical raw waste and treated effluent samples, respectively, after they were analyzed by these two laboratories. It is apparent there has been no significant change in the composition of the samples due to the difference in holding time. The most apparent differences are in the values for low concentrations of metals since the standard metal solutions used in the analyses were of different minimum concentrations in the two laboratories. Agreement between the two laboratories appears to be very good.

Table 6 shows a case where an analysis of two synthetically prepared solutions was made within 24 hours of preparation in Permutit's laboratory and analysis of duplicate samples were made about a week later by the local laboratory. These results also show very good agreement between the two laboratories.

This check was made before the demonstration test started and indicated feasibility of using the two different laboratories, to divide the sample load, for facilitation of a comprehensive and rapid analysis program.

Precipitator Sludge Blowoff

In order to maintain a sludge blanket of relatively constant concentration and depth within the Precipitator, concentrated sludge was removed through a periodic blowoff cycle. The blowoff rate was set and monitored by three different parameters:

(1) The frequency of the blowoff cycle

(2) The duration of the blowoff

(3) The flow rate of sludge, by gravity, through the blowoff collection and discharge lines into a holding sump

Operation and control of the frequency and duration of blowoff cycle is described in Section 4. The settings and their periodic adjustments were recorded routinely on the daily log sheets.

The rate of sludge flow through the blowoff line was not throttled to control the volume of blowoff. All valves on this line were operated in either fully open or fully closed positions. However, as the sludge became denser, the flow rate was influenced by the increased sludge viscosity. Under normal operating conditions, the sludge assumed a concentration of 1.4 to 2.4 percent solids by weight. Manual measurements of sludge flow to the sludge sump indicated the average rate was about 1.59 m^3/hr (7 gpm) during the blowoff period. This was monitored manually about 12 times during the demonstration test and recorded on the log sheets.

The average blowoff rate, on the other hand, takes the whole blowoff cycle (i.e. both time on and off) into consideration and is given as a volume percent of the influent to the Precipitator. The average volume percent blowoff* required during this study has been calculated at 5.9 percent of the influent volume.

In addition to monitoring the volume of blowoff produced, the concentration of the blowoff sludge was routinely determined. Several times or more each week, grab samples of the blowoff were collected and immediately filtered through 0.45 micrometer pore diameter membrane filters. The filters were saved in Petri dishes and labeled for subsequent gravimetric determinations of suspended solids concentrations that existed in the original samples. These suspended solids weighings and final determinations were also made in the Permutit laboratory.

Filter Press Operation

In maintaining the depth of blowoff sludge at a reasonably low level in the sludge sump, the dewatering system was operated about 80% or less of the Precipitator operating time. For some of this filter press pump operating time, however, the pump discharge was recycled back to the sludge sump. This occurred automatically when the sludge level in the sump became too low.

The filtrate flow rate, returning to the second stage neutralization tank, was measured to monitor the rate of sludge flow to the filter press. This measurement was made at various pump speed settings several times a week. Also, the volume of cake produced was measured for several runs of the filter press. Each filtrate rate measurement and filter press unloading was recorded on the log sheets so that the volume of filtrate and cake produced per shift could be calculated.

At regular intervals during the filter press run, the increase in sludge pump discharge pressure was recorded. These recordings were used to develop curves that define the filter press loading capacity as a function of pressure, flow rate and time with the given sludge. A sample of sludge cake was collected and sent to Permutit's laboratory for an analysis of total solids concentration. These samples were collected about once per week for the first three weeks and once per shift over the fourth week.

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*Volume percent blowoff refers to the ratio of the average volume of sludge blowoff to the average volume of influent to the Precipitator.

TABLE 4. COMPARISON OF ANALYSES OF DUPLICATE RAW WASTEWATER SAMPLES BY DIFFERENT LABORATORIES

Metal		Cr^{+6} (mg/l)		Total Cr (mg/l)		Fe (mg/l)		Cu (mg/l)		Zn (mg/l)	
Laboratory		F*	P**	F	P	F	P	F	P	F	P
Date	Sample										
7-14	1:30 PM Grab†	12.3	13	13.3	15	0.67	0.78	0.01	0.02	27.3	29
7-17	1:30 PM Grab	2.4	2.7	3.25	3.1	0.42	0.40	0.01	0.02	16	15
7-18	3:30 PM Grab	6.6	6.6	6.3	7.5	0.80	1.2	0.01	0.02	10.3	14
7-19	1:30 PM Grab	15.8	17	13.3	19	0.53	0.55	0.005	0.01	13	24
7-20	9:30 PM Grab	31.9	33	37.3	36	0.95	1.0	0.18	<0.01	29.3	28
7-26	9:30 PM Grab	95	112	129.5	125	0.40	0.42	0.03	0.03	97.5	97
7-26	5:30 PM Grab	34.2	42	46.3	48	0.65	0.67	<0.01	0.01	39.8	39
7-26	9:30 PM Grab	43.2	52	59.3	60	0.93	0.88	0.02	0.02	67	68
7-26	11:00 PM Grab	47	56	73	71	0.47	0.51	0.02	0.01	68.5	70
7-28	Shift I Comp.††	14.75	16	17	16	0.29	0.24	<0.01	<0.01	17.8	18
7-28	Shift II Comp.	20.75	21	21.8	22	0.19	0.15	<0.01	<0.01	25.8	26
7-31	Shift I Comp.	15.5	10	17.8	19	0.28	0.24	<0.01	0.01	21.5	22
8-8	Shift I Comp.	43.2	41	50.8	50	0.5	0.44	0.01	0.02	41.3	46
8-8	Shift II Comp.	31.3	31	36.3	37	0.7	0.8	<0.01	0.01	36.8	41

*Florence and Hutcheson, Inc. (Local - Paducah, Ky.)

**Permutit Company, Inc.

†Instantaneous grab sample

††Composited Sample over 8 hour shift

TABLE 5. COMPARISON OF ANALYSES OF DUPLICATE FILTER EFFLUENT SAMPLES BY DIFFERENT LABORATORIES

Metal		Cr^{+6} (mg/l)		Total Cr (mg/l)		Fe (mg/l)		Cu (mg/l)		Zn (mg/l)	
Laboratory		F*	P**	F	P	F	P	F	P	F	P
Shift	Sample										
2	Comp.†	<0.01	<0.05	0.04	<0.05	0.15	0.20	<0.01	<0.01	1.5	1.3
3	Comp.	<0.01	<0.05	0.04	<0.05	0.15	0.11	0.01	0.01	0.03	0.03
4	Comp.	<0.01	<0.05	0.04	0.05	0.05	0.07	0.001	0.01	0.04	0.10
5	Comp.	<0.01	<0.05	0.04	0.05	0.11	0.14	0.005	<0.01	0.005	0.03
7	Comp.	<0.01	<0.05	<0.04	<0.05	0.10	0.09	0.15	<0.01	0.01	0.06
14	Grab ††	0.01	<0.05	0.65	0.68	<0.05	<0.05	<0.01	<0.01	<0.01	0.01
14	Comp.	0.02	<0.05	0.48	0.60	0.06	<0.05	<0.01	<0.01	0.01	0.01
15	Grab	0.02	<0.05	0.04	0.17	<0.05	<0.05	<0.01	<0.01	<0.01	<0.01
15	Comp.	0.02	<0.05	0.48	0.86	0.06	0.07	<0.01	<0.01	0.01	0.02
18	Comp.	<0.01	<0.05	0.04	<0.05	0.06	0.06	0.01	<0.01	0.023	0.02
19	Comp.	<0.01	<0.05	<0.04	<0.05	0.15	0.09	<0.01	<0.01	0.026	0.03
20	Grab	<0.01	<0.05	<0.04	<0.05	0.06	0.06	<0.01	<0.01	0.02	0.03
20	Comp.	<0.01	<0.05	<0.04	<0.05	0.36	0.28	<0.01	<0.01	0.06	0.08
32	Grab	0.01	<0.05	0.04	0.05	0.05	<0.05	<0.01	<0.01	<0.01	<0.01
32	Comp.	<0.01	<0.05	<0.04	<0.05	0.5	0.40	<0.01	<0.01	0.03	0.04
33	Grab	<0.01	<0.05	<0.04	<0.05	0.07	<0.05	<0.01	<0.01	0.01	0.01
33	Comp.	<0.01	<0.05	0.04	<0.05	0.01	0.08	<0.01	<0.01	0.03	0.02

*Florence and Hutcheson, Inc. (Local-Paducah, Ky.)
**Permutit Co., Inc.
†Composited sample over 8 hour shift
††Instantaneous grab sample

TABLE 6. COMPARISON OF METAL ANALYSES OF SYNTHETIC SOLUTIONS BY DIFFERENT LABORATORIES

Sample	Laboratory	mg/l Fe	mg/l Cu	mg/l Zn	mg/l Cr	mg/l Cr^{+6}
#1	Florence + Hutcheson Analyst #1	0.67	0.23	18.6	19.0	19.4
	Florence + Hutcheson Analyst #2	0.60	0.23	21.8	19.4	20.2
	Permutit	0.51	0.24	21	20	20.5
#2	Florence + Hutcheson Analyst #1	16.0	0.01	0.64	0.09	0.04
	Florence + Hutcheson Analyst #2	14.8	0.01	0.60	0.08	0.04
	Permutit	12	0.01	0.65	0.05	0.03

SECTION 6

RESULTS AND DISCUSSION

EFFECTIVENESS OF WASTEWATER TREATMENT PROCESS

Variations in the Raw Wastewater

The wastewater treatment system at Holley has been designed to handle the following maximum ranges of raw wastewater components occurring simultaneously; zinc - 30 to 80 mg/l, copper - 0.1 mg/l, total chromium - 50 to 80 mg/l, and a maximum flow of 7.9 m^3/hr (35 gpm). These have been specified as the "worst case" conditions for the metal finishing process wastewater discharge.

During the beginning of this demonstration study, the wastewater flow rate ranged between 4.2 and 6.7 m^3/hr (19 and 30 gpm). Minor modifications in the rinse water rate controllers minimize these flow fluctuations to obtain a normal flow rate between 5.6 and 6.1 m^3/hr (25 and 27 gpm). Figure 4 shows the average flow fluctuations as they occured on a shift-by-shift basis. In this, and most of the following figures, time is plotted in a sequence of the 38 shifts during which these observations were made. Shutdown time between the shifts in this sequence is omitted.

During many of these shifts, the concentration variations of the wastewater components were observed within the range of the worst case conditions. The raw wastewater samples that were collected and analyzed, as described in Section 5, indicate that wide variations in wastewater composition occurred. These results are shown in Figures 5, 6, 7, 8, 9, and 10, for hexavalent chromium and zinc, total chromium, pH value, total suspended solids, total iron, and copper, respectively.

The variations were due to fluctuations in metal finishing process operations, including occasional dumps of rinse tanks and partial dumps of concentrated process tanks. On the basis of shift averages, the concentrations of hexavalent chromium and zinc varied from a maximum of 85 mg/l Cr^{+6} and 90 mg/l Zn to a minimum of 3 mg/l of Cr^{+6} and 3 mg/l Zn. The pH varied between 5.0 and 6.8 and total suspended solids varied between 5 mg/l and 100 mg/l.

Quality of Treated Wastewater Effluent

As described in Section 5, the composite filter effluent samples collected over a shift period were analyzed for metals and suspended solids. The analytical results obtained for the filtered effluent and the raw wastewater are shown in Figures 11, 12, 13, 14, and 15. These figures compare metal concentrations, in the treated and untreated wastewater , for total Cr, Cr^{+6},

Zn, Fe and Cu, respectively. The results indicate that this system did produce desired effluent quality despite wide variations in the influent raw wastewater.

In addition, these results suggest that this system does have a limited tolerance when subjected to abrupt changes of higher intensity. During the demonstration period, a partial dump of concentrated process solution did occur due to unfamiliarity of the plant's operating personnel with the discharging of plant waste solutions to the appropriate receiving sump. This resulted in an increased loading of metals, significantly higher than the design maximum levels, to the treatment system. Consequently, the effluent quality produced was also affected. However, of all the metals monitored, only total chromium was significantly affected, whereas the values for zinc and hexavalent chromium were still below the specified limits during these periods.

The increases in treated effluent total chromium were apparently due to excessive trivalent chromium carryover from the Precipitator and, consequently, from the filter. However, the excess ferrous sulfide, fed to the influent, was sufficient to effectively reduce hexavalent chromium, precipitate zinc and maintain these parameters in the desired range.

A comparison of the shift average values obtained for the different metals before and after "Sulfex"TN treatment is given in Table 7. This summarizes, on a monthly average basis, the effectiveness of the "Sulfex"TN process in removing heavy metals from the raw wastewater to meet even the most stringent limits that have been defined in Section 4. The most stringent limit for each parameter is the lowest of the values listed in Table 1, Table 2, or Table 3.

TABLE 7. AVERAGE WASTEWATER COMPOSITIONS DURING "SULFEX"TN STUDY

Metal	Untreated* influent (mg/l)	Treated* effluent (mg/l)	Most stringent state or city limit for Paris, Tenn. STP (mg/l)
Zn	39.5	<0.07†	0.04
Fe	0.52	0.10	-
Cu	<0.01	<0.01	0.5
Cr	32.3	<0.04	1.0
Cr+6	25.6	<0.01	0.05
TSS	46.5	<1.0	<1500

*Average of 22-day test monitoring period (7/11 to 8/11/78).

†This value is the calculated maximum average possible for all effluent zinc analysis during this period. As Figure 13 illustrates, elimination of the atypical first sample value (1.5 mg/l Zn) gives an average effluent zinc of less than 0.03 mg/l.

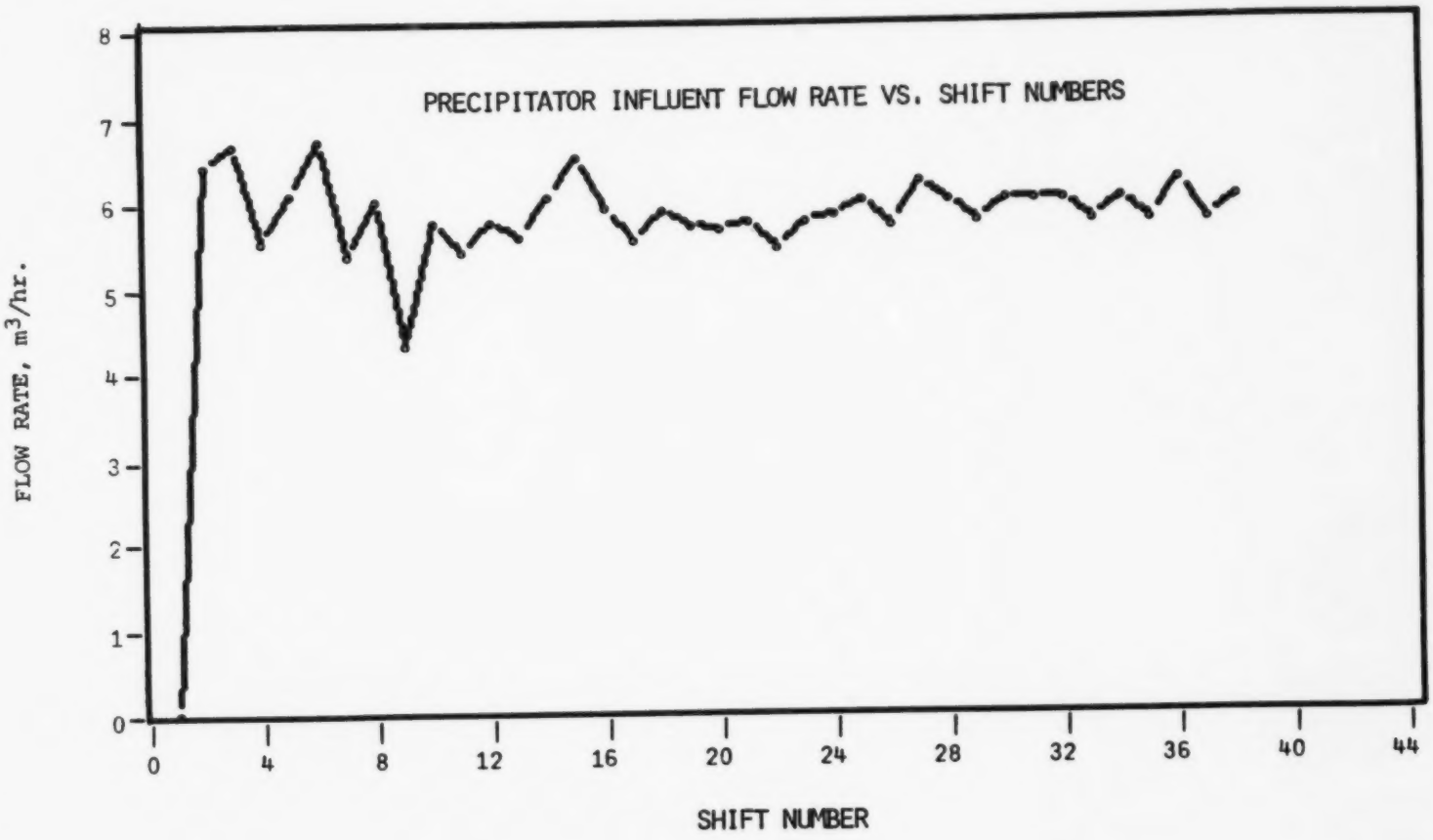

Figure 4. Influent flow rate to Precipitator as a function of time.

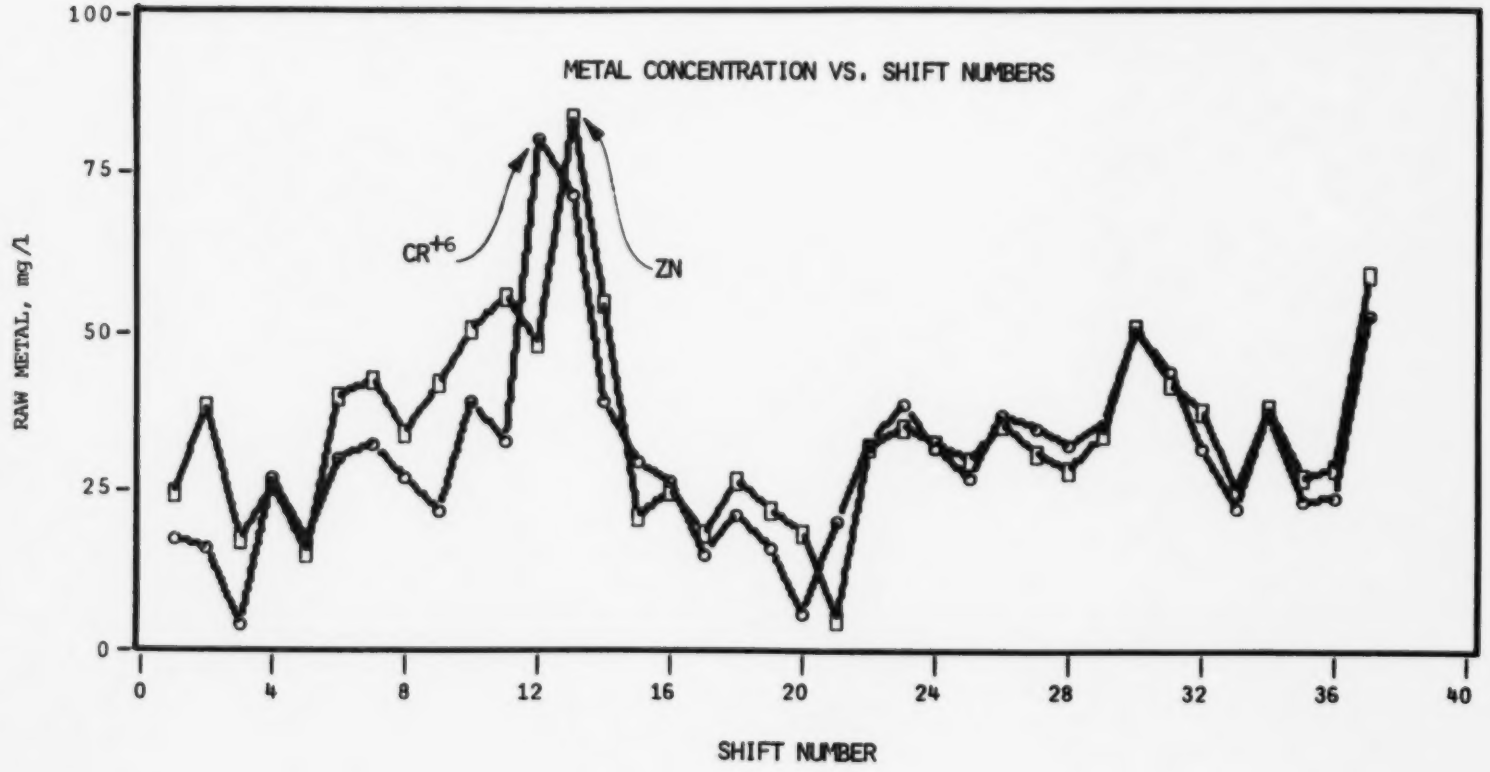

Figure 5. Average concentration of Cr^{+6} and Zn in untreated wastewater as a function of time.

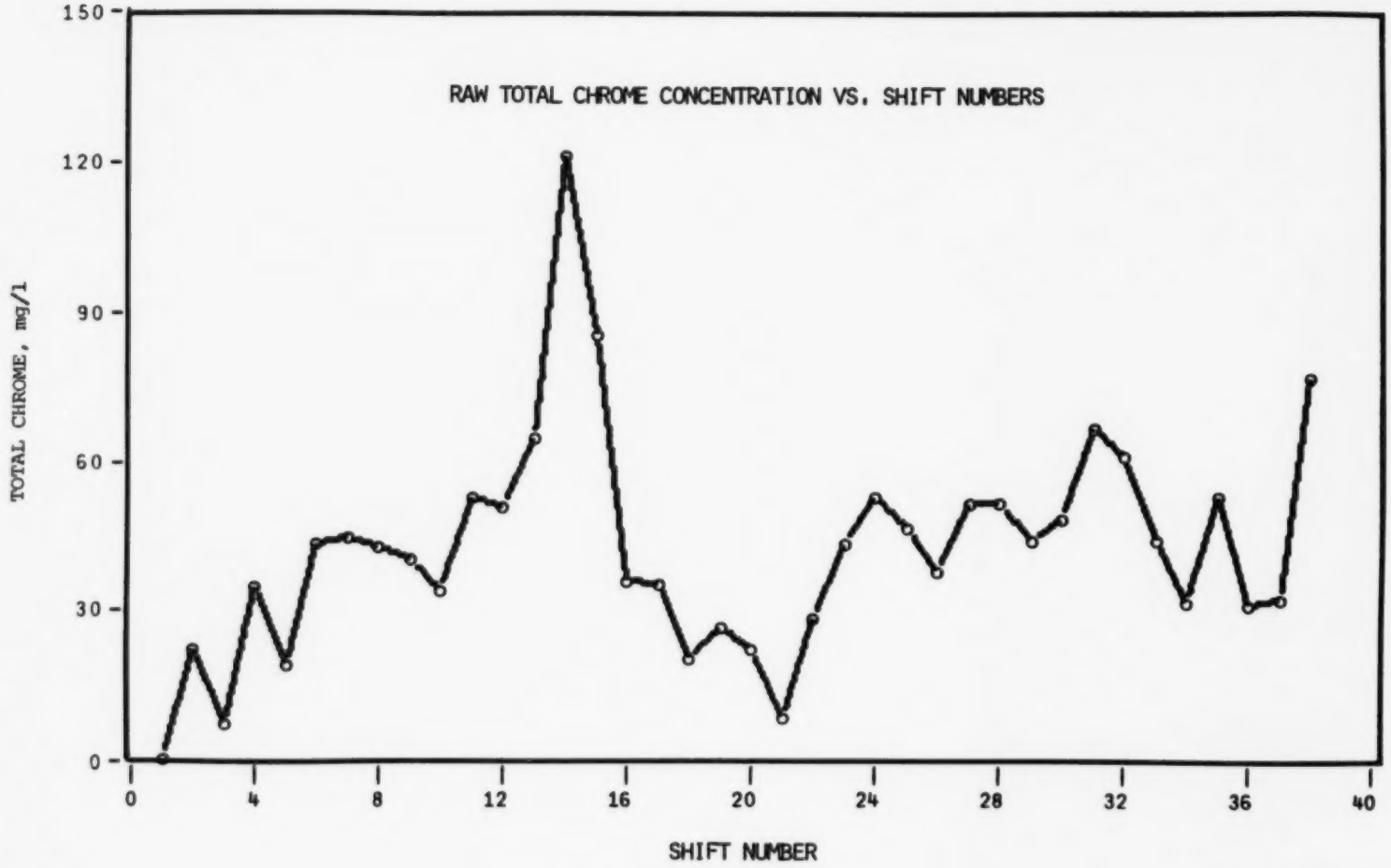

Figure 6. Average concentration of total chrome in raw influent as a function of time.

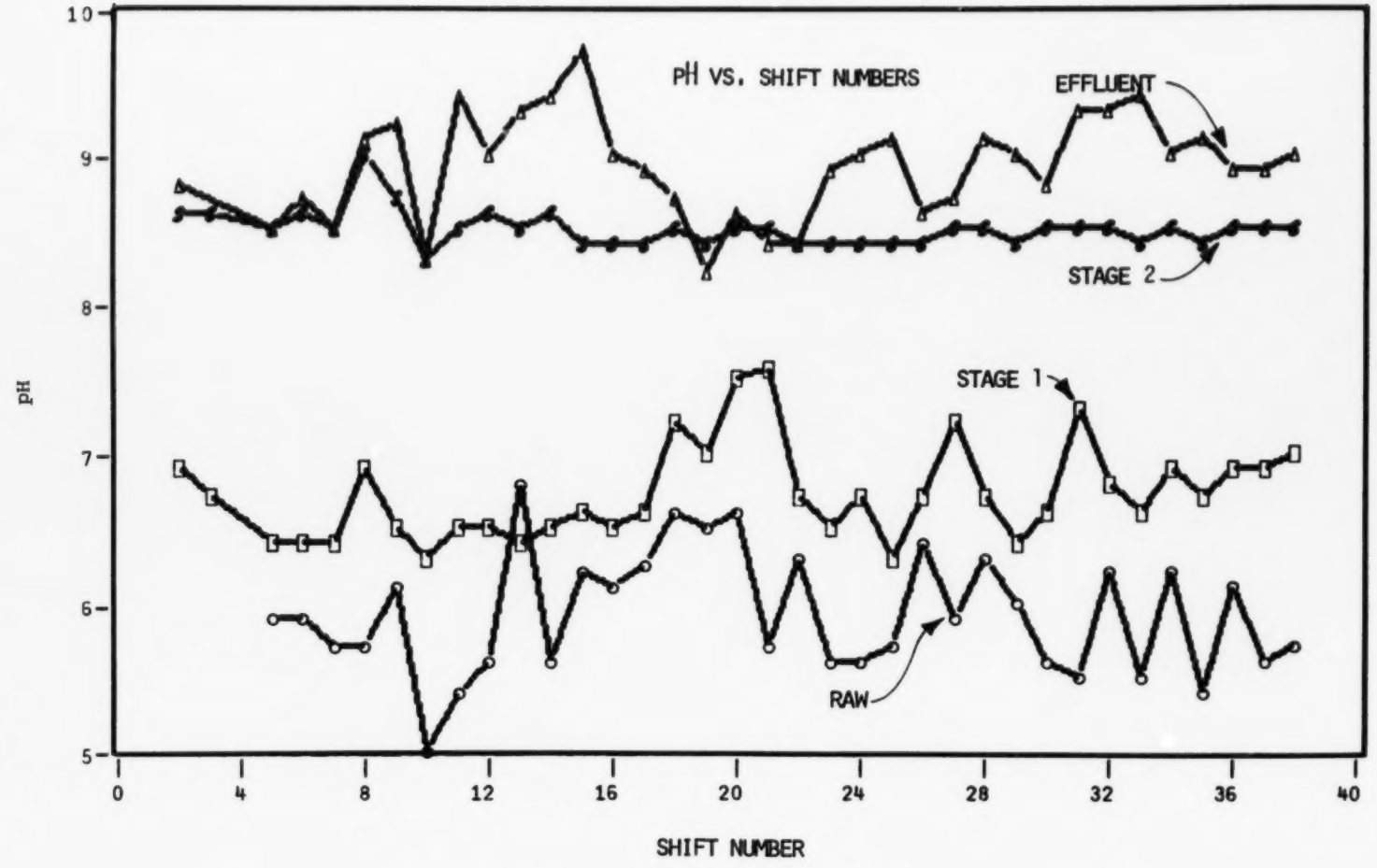

Figure 7. Average pH values of wastewater treatment process steps as a function of time.

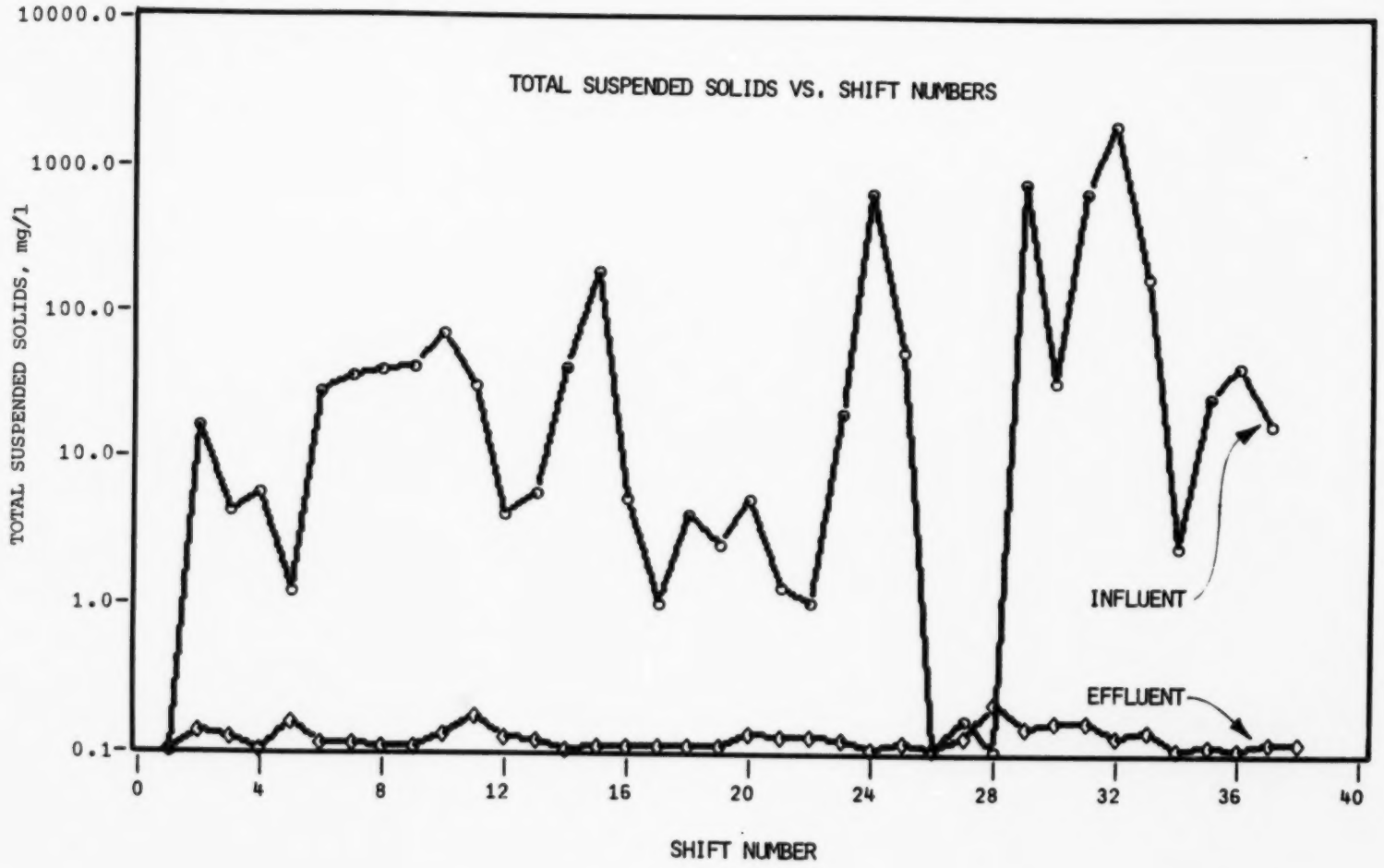

Figure 8. Average concentration of total suspended solids in untreated influent and treated effluent as a function of time.

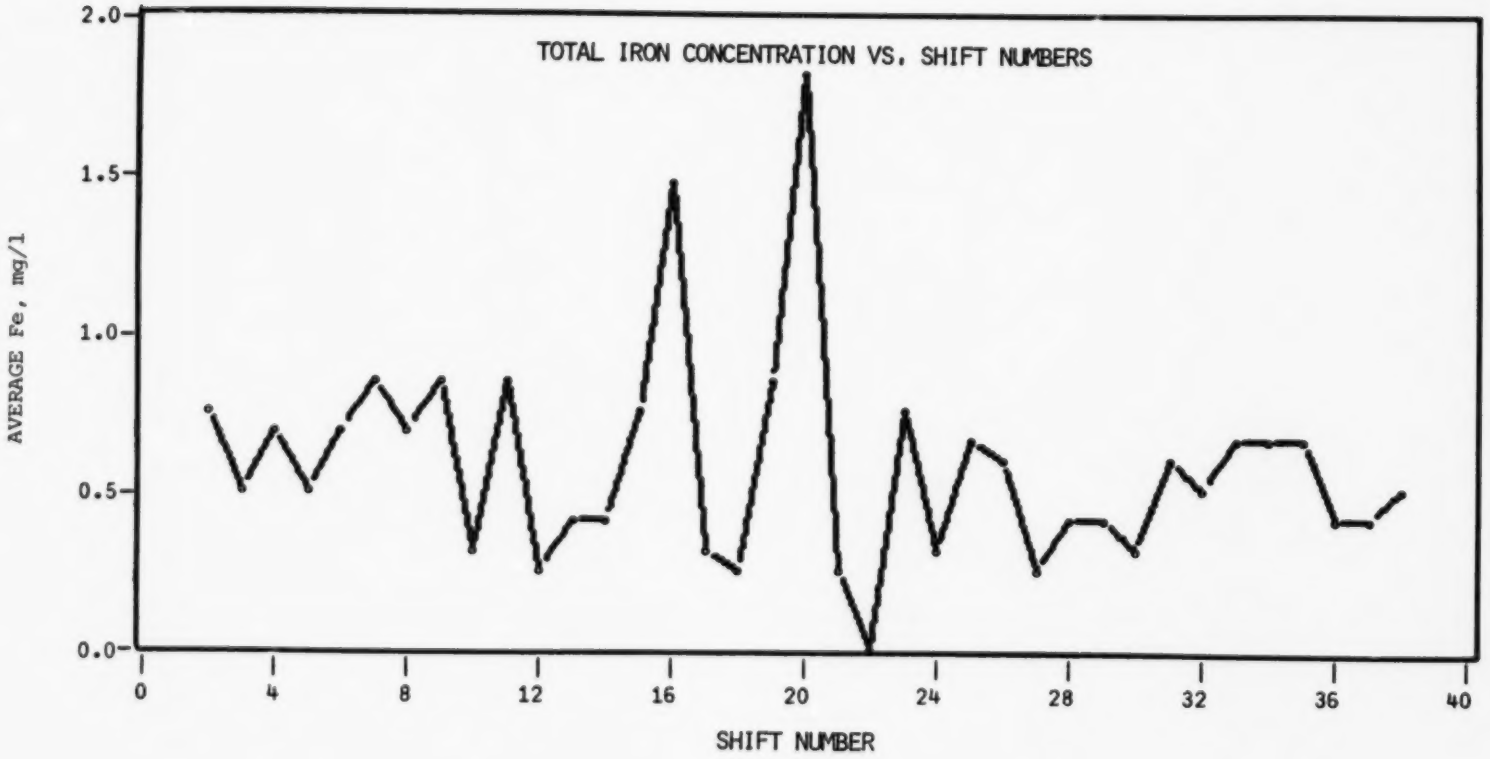

Figure 9. Average concentration of total Fe in untreated wastewater as a function of time.

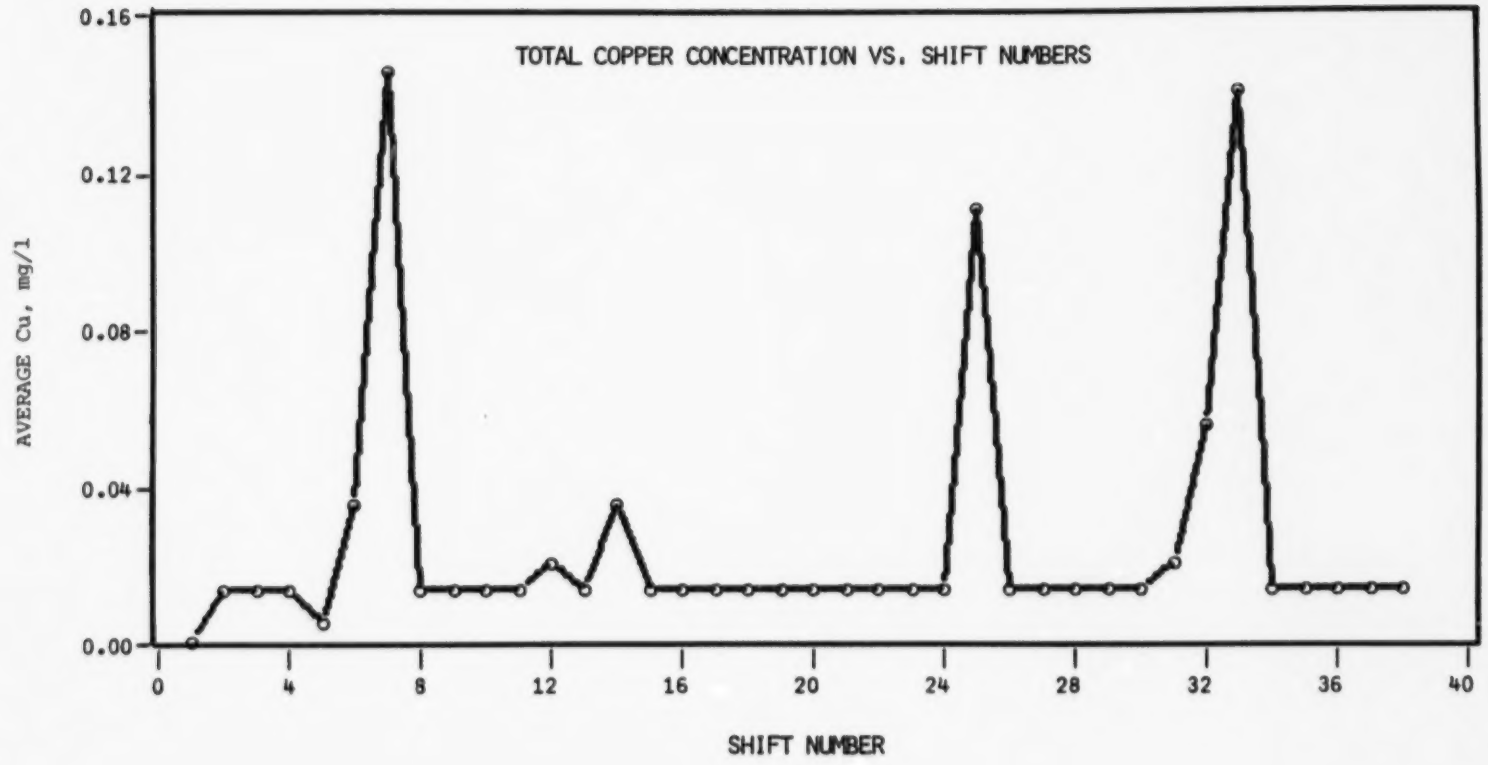

Figure 10. Average concentration of Cu in untreated wastewater as a function of time.

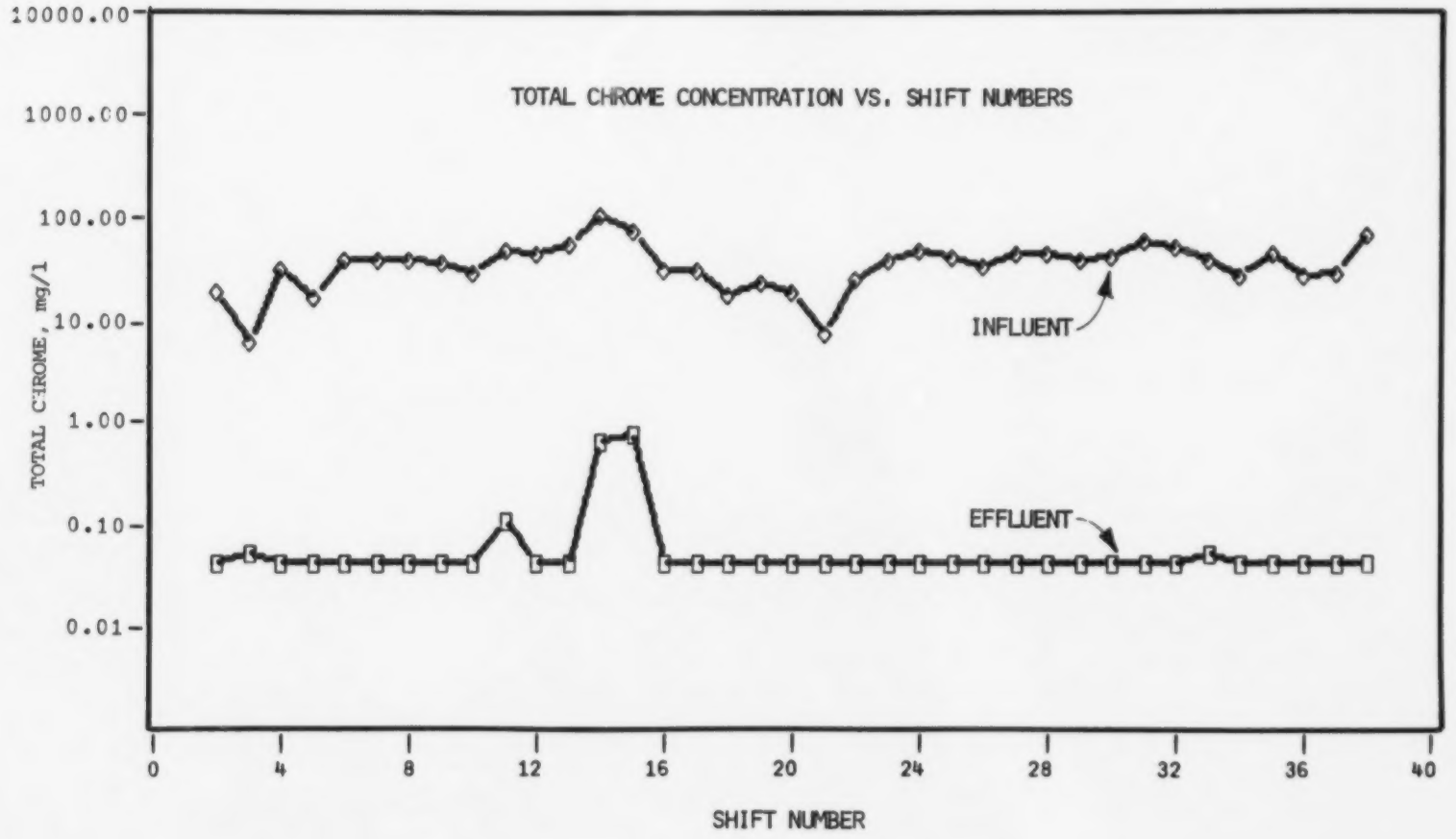

Figure 11. Average concentration of total Cr in untreated wastewater and treated effluent as a function of time.

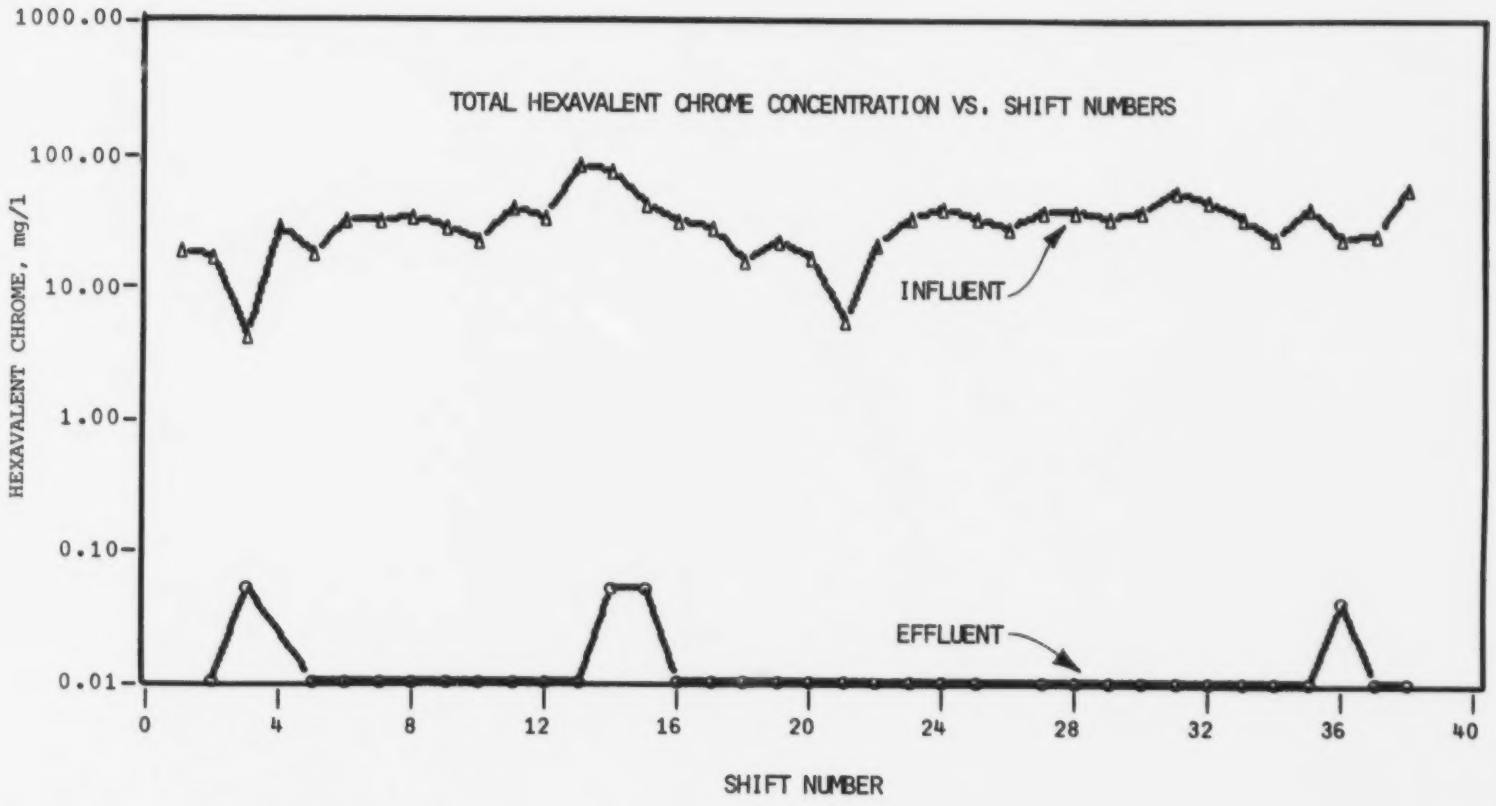

Figure 12. Average concentration of Cr^{+6} in untreated wastewater and treated effluent as a function of time.

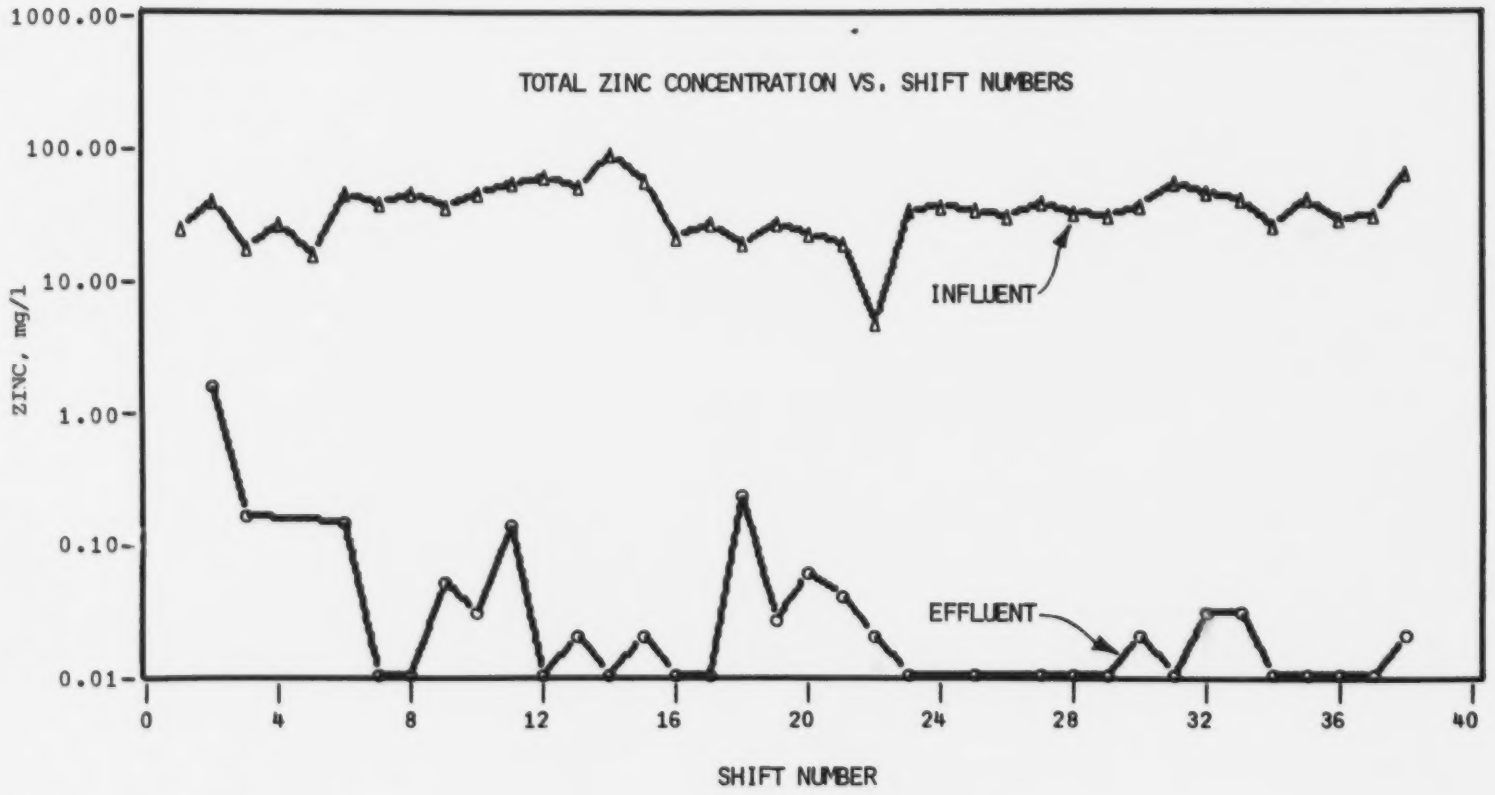

Figure 13. Average concentration of total Zn in untreated wastewater and treated effluent as a function of time.

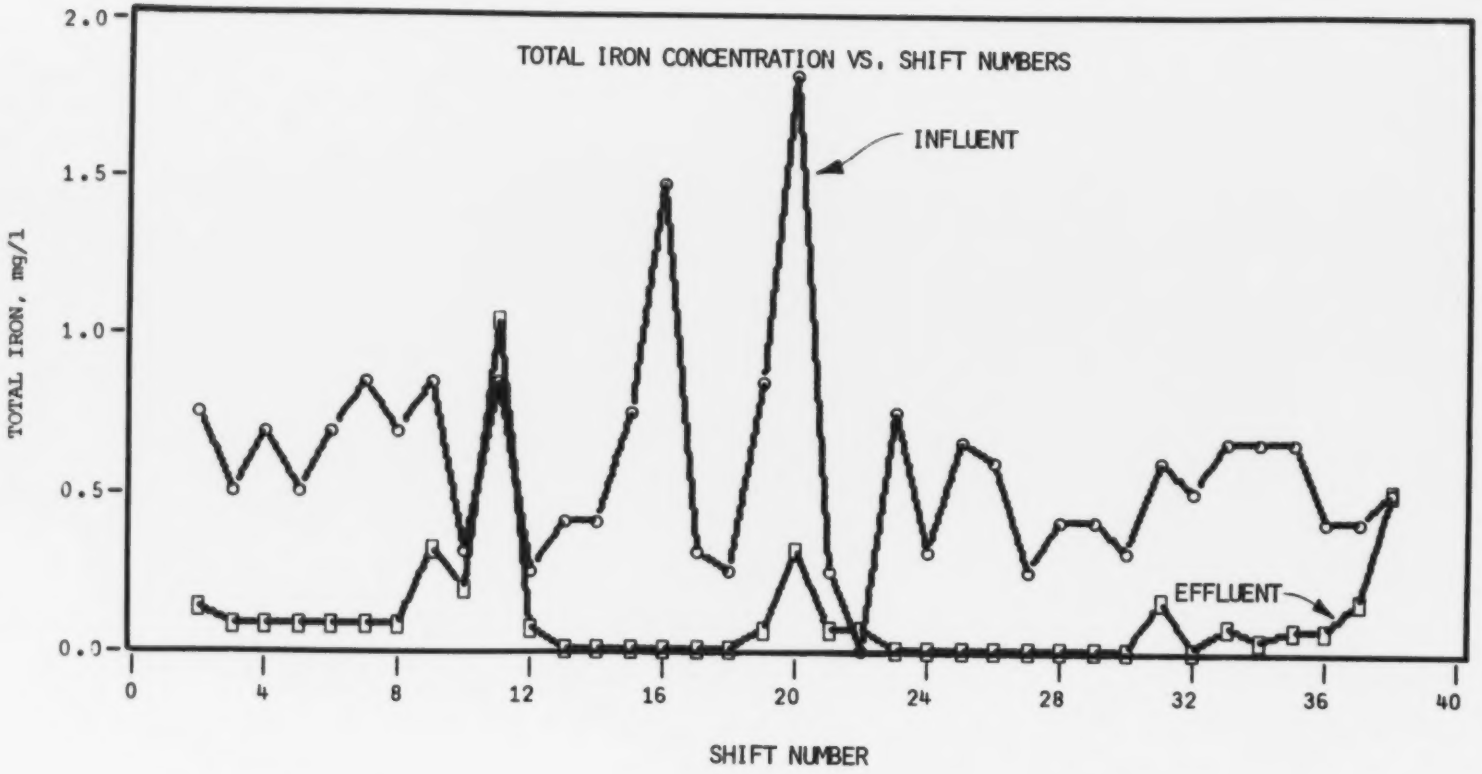

Figure 14. Average concentration of total Fe in untreated wastewater and treated effluent as a function of time.

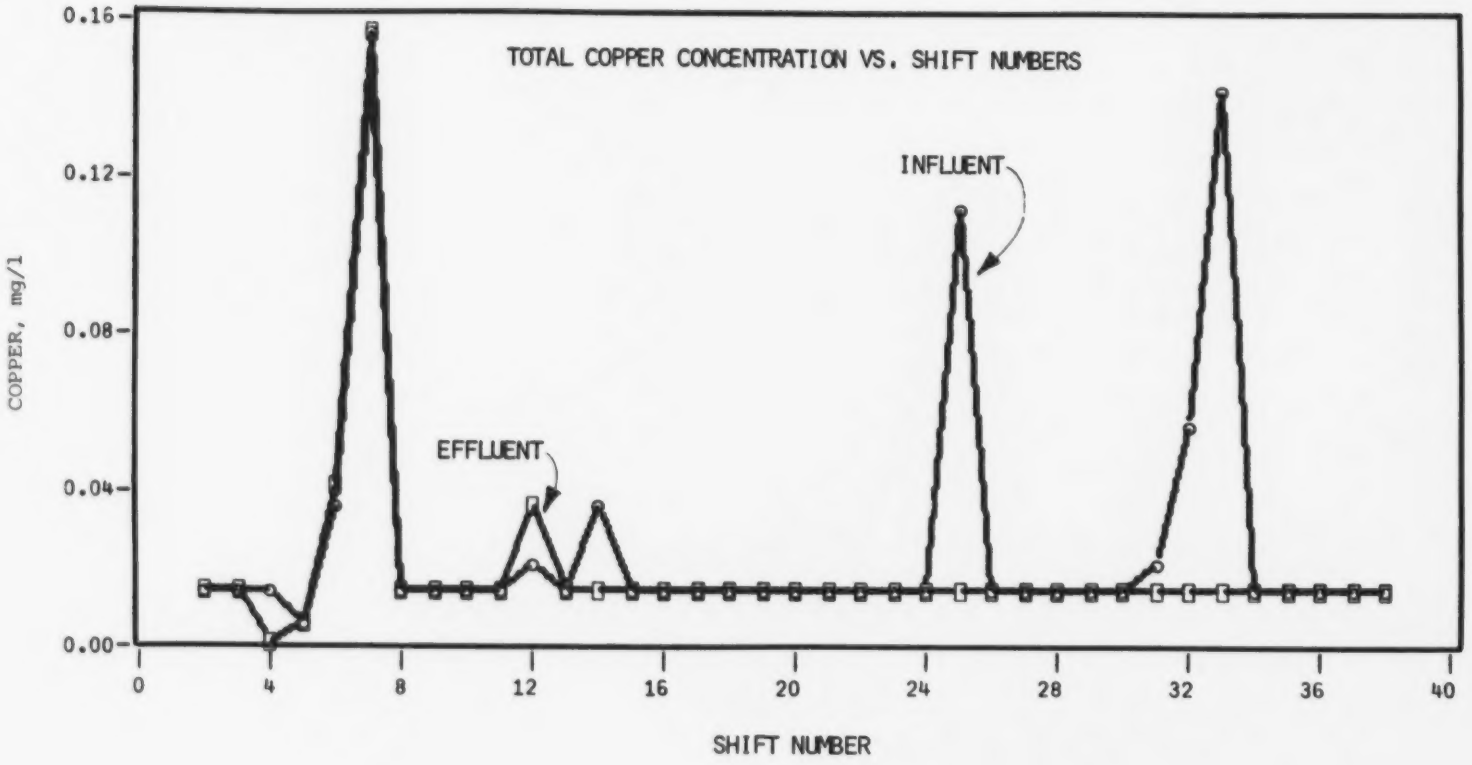

Figure 15. Average concentration of total Cu in untreated wastewater and treated effluent as a function of time.

Besides the normal filtered effluent parameters already discussed, a weekly spot check for an oil and grease analysis was made. Results show that the oil and grease values were normally below detectable levels except on one occasion when it was 1.1 mg/l. Although raw wastewater samples were not analyzed for oil and grease, there was no visually apparent oil or grease present in the influent wastewater.

CONTROL OF OPERATIONAL PARAMETERS

Control of pH

One of the most important factors in meeting the desired effluent criteria for dissolved metals was maintaining the pH of the wastewater in the 8.0-9.0 range during the reaction and separation steps. To accomplish this, a two-stage pH adjustment system was provided. The pH value of the raw wastewater and the Precipitator effluent were monitored throughout the demonstration test.

The first stage of the pH control system was automatically held in the 6.5 to 7.2 pH range. The only time this stage didn't operate in this pH range was when a tank of phosphoric acid was dumped. In this case, when the second stage pH control detected the drop below pH 8.0, it automatically went into recycle operation of the neutralization system until the pH was again above 8.0.

Figure 7 illustrates the fluctuation of pH for each stage as a function of time. This figure shows pH changes in the raw influent, first stage neutralization tank, second stage neutralization tank, and the Precipitator effluent. Each point on these graphs represents the averaged pH values recorded per shift for the location in question. Only on one occasion did the Precipitator effluent pH vary to a level significantly higher than desirable (i.e. >9.5). This high pH variation is attributed to the improper dumping of a phosphoric acid solution containing a high hexavalent chromium concentration. This increased the pH of the Precipitator effluent due to the chemical reduction of hexavalent chromium to trivalent chromium which has the effect of producing excess hydroxyl ions as follows:

$$CrO_4^{-2} + 4H_2O + FeS = S^o + Fe(OH)_3 + Cr(OH)_3 + 2OH^- \quad (1)$$

hexavalent chromium	ferrous sulfide	sulfur	ferric hydroxide	chromic hydroxide	hydroxyl ions

Chemical Consumption

As described in Section 4, three different chemical preparations were continuously fed at various stages of the treatment process. These were lime, ferrous sulfide, and polyelectrolyte. The lime was prepared as a slurry and fed to the neutralization system. The ferrous sulfide was also prepared as a slurry and was fed to the influent flume of the Precipitator where it first intermixed with the neutralized wastewater. A solution of polyelectrolyte was fed to the mixing zone of the Precipitator by way of a separate distributor.

The consumption of all three chemical preparations was constantly monitored by measuring the amount of drawdown that occurred during specific time periods. The quantities of each chemical that were used for each shift during this demonstration were determined. The chemical usage, on a shift-by-shift basis, is shown in Figures 16, 17, and 18 for ferrous sulfide, polyelectrolyte, and lime, respectively.

The usage of ferrous sulfide fluctuated considerably throughout the first 20 shifts (i.e. 2.5 weeks). This was due to fluctuating demand caused primarily by two problems:

1. The flow rate of the wastewater from the plant was more variable during this period because the different operators of the Udylite system tended to control rinse rates at different levels for the first week or two. This problem was overcome by instructing the operators of the Udylite system to run the rinses at more uniform rates. Figure 4 shows how the influent flow to the Precipitator fluctuated during this study.

2. Initially, periodic discharges of concentrated process solutions were not made to the proper holding tank, but were allowed to go directly to the first stage neutralization tank. This caused high increases in treatment chemical demand for several hours after each discharge was made. After this problem was pointed out, the discharges were made to the spent bath sump provided for this purpose, from which they were slowly bled to the waste treatment system. When spent bath discharges were properly made, sudden increases in chemical demand were not observed.

The actual usage of ferrous sulfide, shown in Figure 16, was controlled according to routine jar test demand results that gave relatively quick (30 to 45 minutes) estimates of the ferrous sulfide dosages needed for the Precipitator operation. The theoretical requirement for ferrous sulfide was determined by laboratory analytical methods of the untreated waste. These analyses required four to six hours after delivery of samples to the laboratory before the results were ready. This made it impractical to try to control the ferrous sulfide feed rate by laboratory metal analyses.

Since the jar tests for ferrous sulfide demand did not use a sludge blanket technique (i.e. sludge recirculation), but the Precipitator did have a sludge blanket, the real ferrous sulfide demand by the system was considerably less than the jar tests have indicated. Results of previous EPA demonstration test for "Sulfex"TN* show that when a concentrated sludge blanket is present, the process becomes more effective and efficient in removing the residual dissolved metals.

Also, the real ferrous sulfide demand required is normally higher than the theoretical demand as calculated from the wastewater analyses. Excess ferrous sulfide dosage is necessary to overcome slow reaction kinetics caused by low metal concentration, complexing agents, and other interferences.

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*Schlauch, R. M. and A. C. Epstein. Treatment of Metal Finishing Wastes by Sulfide Precipitation. EPA-600/2-77-049, U.S. Environmental Protection Agency, Cincinnati, Ohio, Feb. 1977. Figure 1, p. 17 and Figure 5, p. 34.

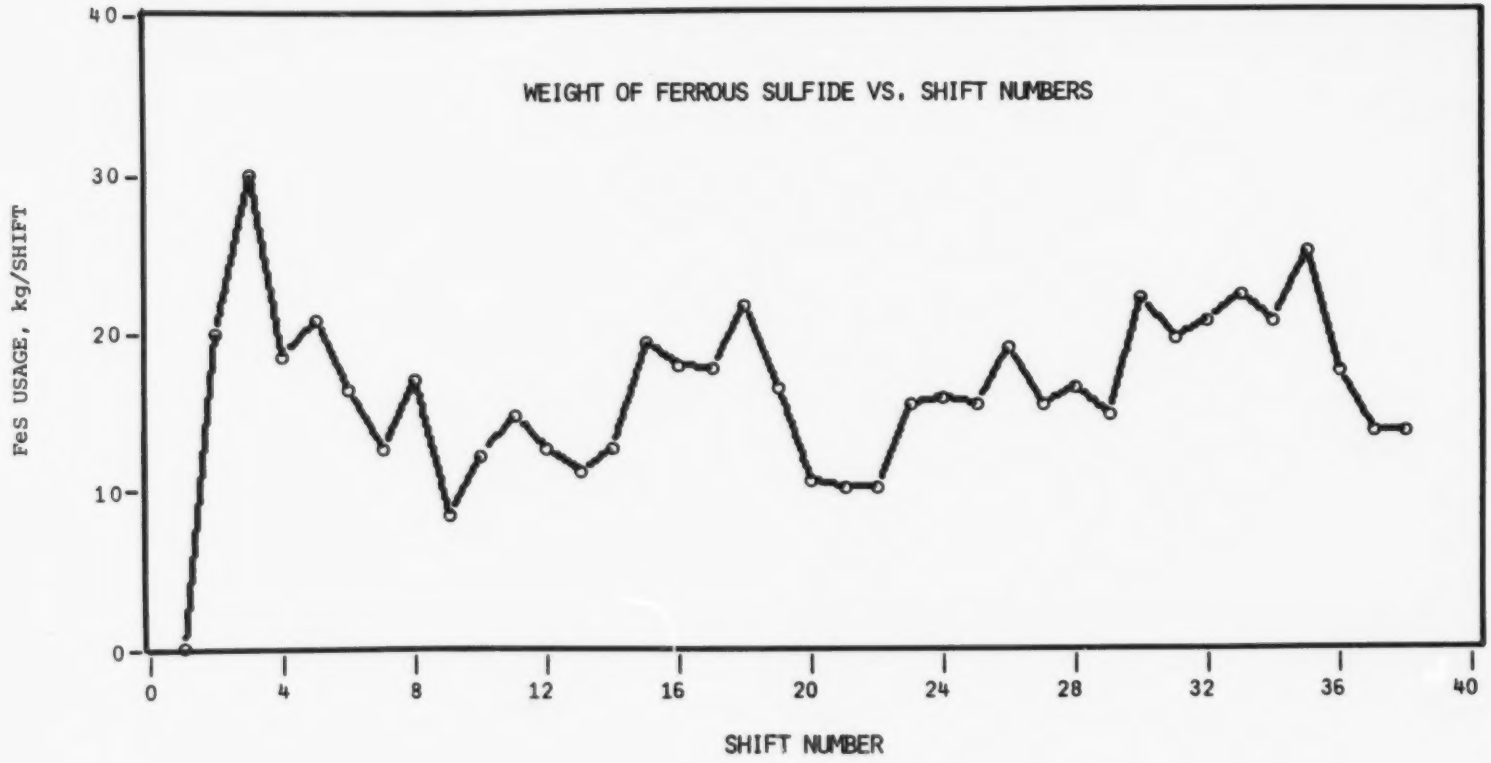

Figure 16. Ferrous sulfide usage as a function of time.

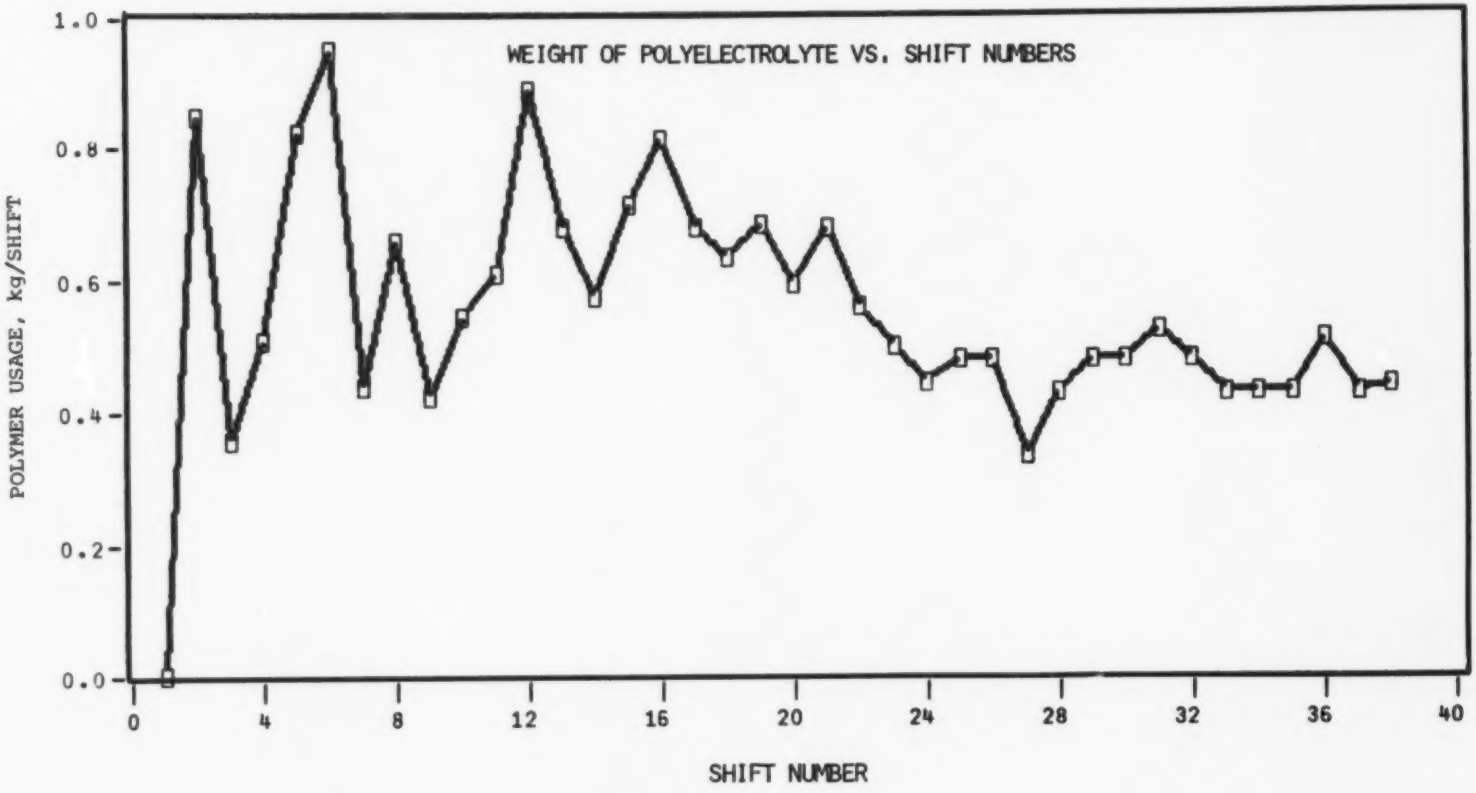

Figure 17. Polyelectrolyte usage as a function of time.

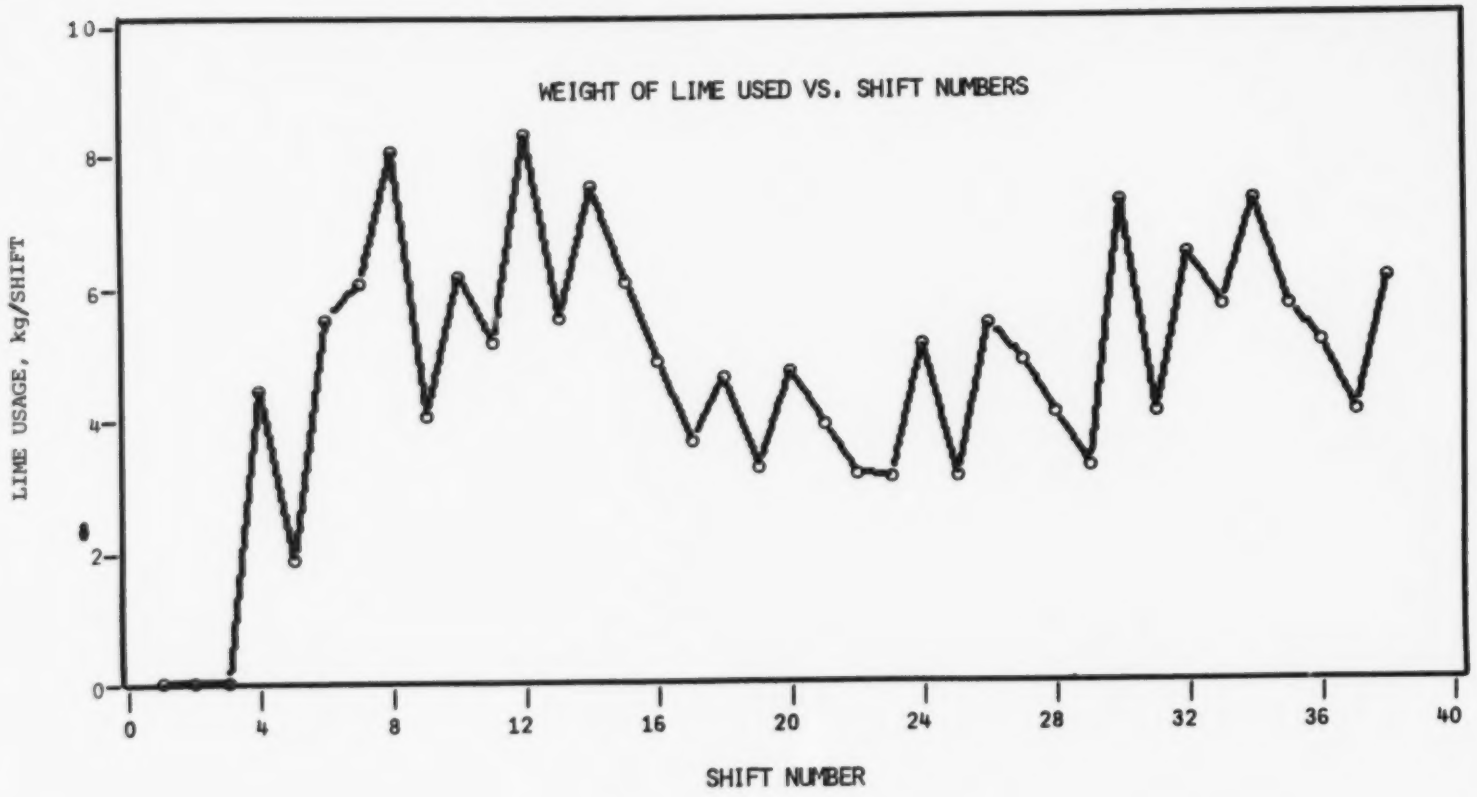

Figure 18. Lime used for neutralization as a function of time.

The polyelectrolyte usage also fluctuated considerably over the first twenty shifts, as shown in Figure 17. This was due to fluctuations in both flow rate and ferrous sulfide usage. In order to effectively coagulate the suspended solids in the Precipitator, the polyelectrolyte concentration has to be relatively proportional to the ferrous sulfide concentration. In this test, the optimum polyelectrolyte dosage was found to be about 1 part by weight of polymer to 40 parts by weight of ferrous sulfide. Over the last eighteen shifts, when flow rate fluctuations and improper spent bath discharging operations were corrected, the polyelectrolyte usage leveled out to about 454 grams (1.0 pound) per shift.

Unlike ferrous sulfide and polyelectrolyte, the usage of lime is not totally dependent upon the metal loadings in the influent waste. The consumption of lime also depends on the acidity and alkalinity of the wastewater. Figure 18 shows the variation in lime consumed per shift for neutralizing the raw wastewater. Fluctuations shown for the lime demand are more pronounced than either the ferrous sulfide or the polyelectrolyte flcutuations that occurred. However, it is also seen that the greatest fluctuations in lime demand occurred during the first twenty shifts as they did for ferrous sulfide and polyelectrolyte.

Control of Sludge Blanket as a Sulfide Reservoir

The sludge blanket that forms in the reaction and settling zones of the Precipitator is composed mainly of metal sulfides, hydroxides, phosphates, and carbonates as well as unreacted ferrous sulfide. The value of this unreacted, stored ferrous sulfide in the blanket comes into play when the demand for sulfide in the influent exceeds the supply of ferrous sulfide to the influent. Then, it is important to have a concentrated mass of fluidized solids in the blanket zones of the Precipitator to store as much active ferrous sulfide, in reserve, as possible.

Monitoring of the sludge blanket concentration was performed by the settling tests described in Section 5. These tests measured the periodic concentration changes in the blanket on the basis of volume percent solids. Figure 19 shows the average volume concentration of solids obtained for the mixing and settling zones, as a function of time, on a shift-by-shift basis. Note that the changes in concentration of mixing zone solids (reaction zone) varied directionally with changes in settling zone concentration, but to a lesser degree. The normal variation of solids volume concentration in the mixing zone was from about 25 volume percent to about 75 volume precent. The normal concentration change in the settling zone varied from about 25 volume percent to about 85 volume percent.

To relate volume percent solids to a more widely used representation of solids concentration, the gravimetric suspended solids concentrations (mg/l) of a number of samples of mixing and settling zone blankets were analyzed. Figure 20 shows the relationship that has been developed for relating volume percent solids to mg/l suspended solids for this system.

It is clear that the relationship is not linear but that a wide range of volume percent values exist over a rather narrow range of mg/l suspended solids concentrations. It is shown that the average suspended solids concentrations that normally existed during the study were about 6000 to 6500 mg/l in the mixing zone and from 6000 to 8000 mg/l in the settling zone. It was also found, as previously discussed, that the normal concentration of suspended solids in the concentrator (at the bottom of the settling zone) ranged from about 14,000 up to about 24,000 mg/l.

With the high concentrations of fluidized solids in the mixing and settling zones, high concentrations of active ferrous sulfide were available for chemically reacting with residual hexavalent chromium and zinc. The blanket solids provide crystallization sites for increasing the rate of metal precipitation within the Precipitator reaction zone.

Reference to Figure 21 will show how the blanket acted as a reservoir for ferrous sulfide. The more densely shaded areas indicate periods when ferrous sulfide, actually fed to the influent, was not completely consumed by the existing demand in the influent. The excess ferrous sulfide concentration (i.e. the height of the dark shaded area) was accumulated in the blanket during these periods. (It is estimated that ferrous sulfide thus stored in the blanket was available for about 19 hours before being removed via blowoff operations.)

The more sparsely shaded areas represent periods when no excess ferrous sulfide was being added to the Precipitator influent. Then, the ferrous sulfide stored in the blanket was utilized to make up for the insufficient dosage supplied to the influent.

Figure 21 was developed from Figure 22 which shows how the actual ferrous sulfide supply varied with time as compared to the jar test demand observed for influent waste. By comparison, Figure 23 shows how the theoretical ferrous sulfide demand (calculated from influent chemical analyses) compared with the ferrous sulfide actually supplied. Also, for sake of comparison, Figure 24 shows how the jar test ferrous sulfide demand compared with the theoretical ferrous sulfide demand.

Figure 25 relates average jar test ferrous sulfide demand as a percentage of the average theoretical demand on a shift-by-shift basis. The jar test demand normally varied from about 200% to about 500% of the theoretical demand or, in other words, it averaged about 3.4 times as high. If sludge blanket conditions (i.e. sludge recirculation) would have been practiced in the jar tests, the resultant ferrous sulfide demand would have been closer to the theoretical demand. Obviously, the ferrous sulfide dosages fed to the system throughout this demonstration test could have been maintained at somewhat lower levels since the final effluent hexavalent chromium and zinc concentrations were maintained at levels significantly less than the required limits.

Figures 12 and 13 show the residual concentrations, in filtered effluent, for hexavalent chromium and zinc, respectively. These plots show the hexavalent chromium and zinc values were always well below the guaranteed 0.1 mg/l and 1.0 mg/l respective effluent limits that were set for this system.

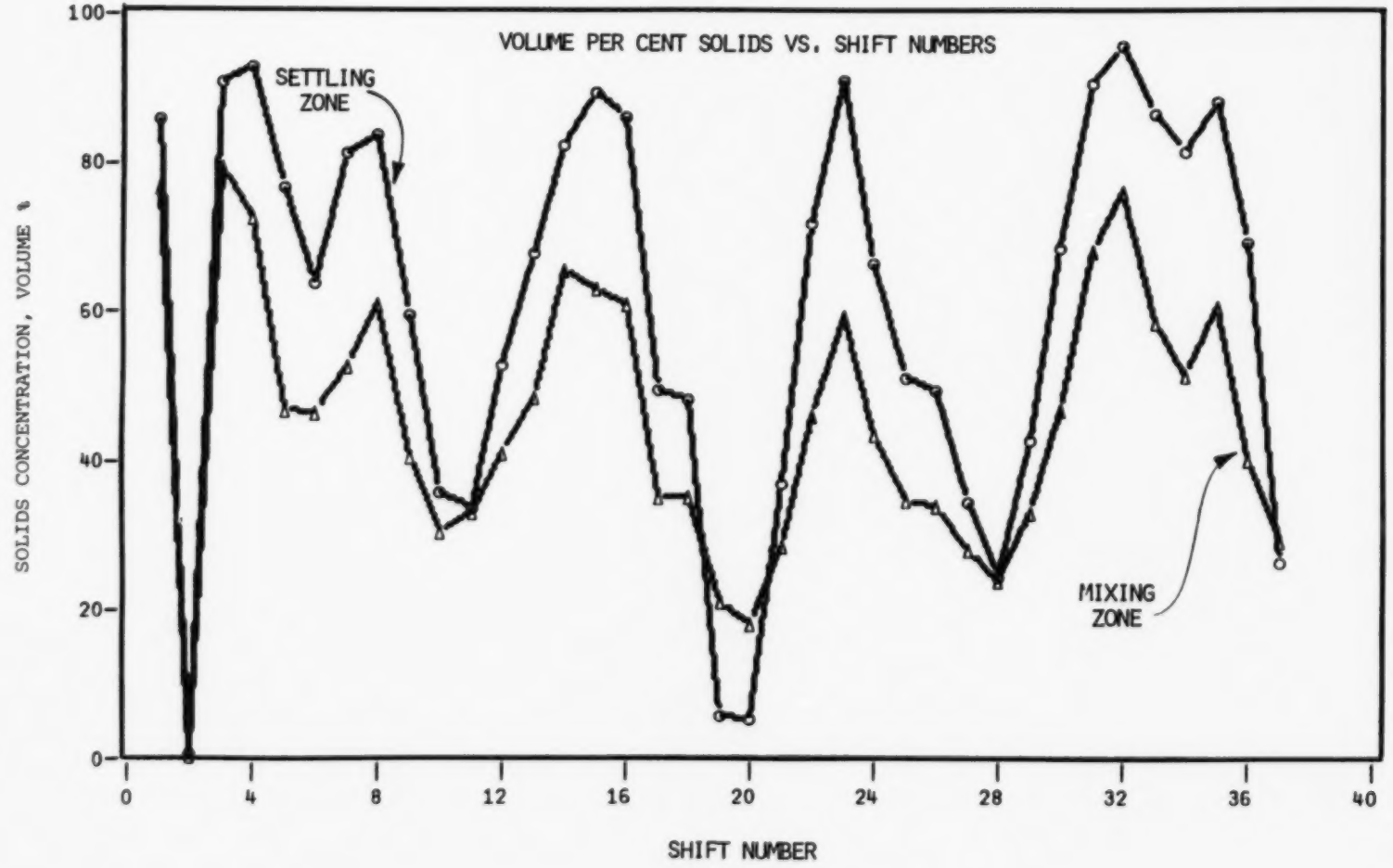

Figure 19. Average blanket solids concentration in Precipitator as a function of time.

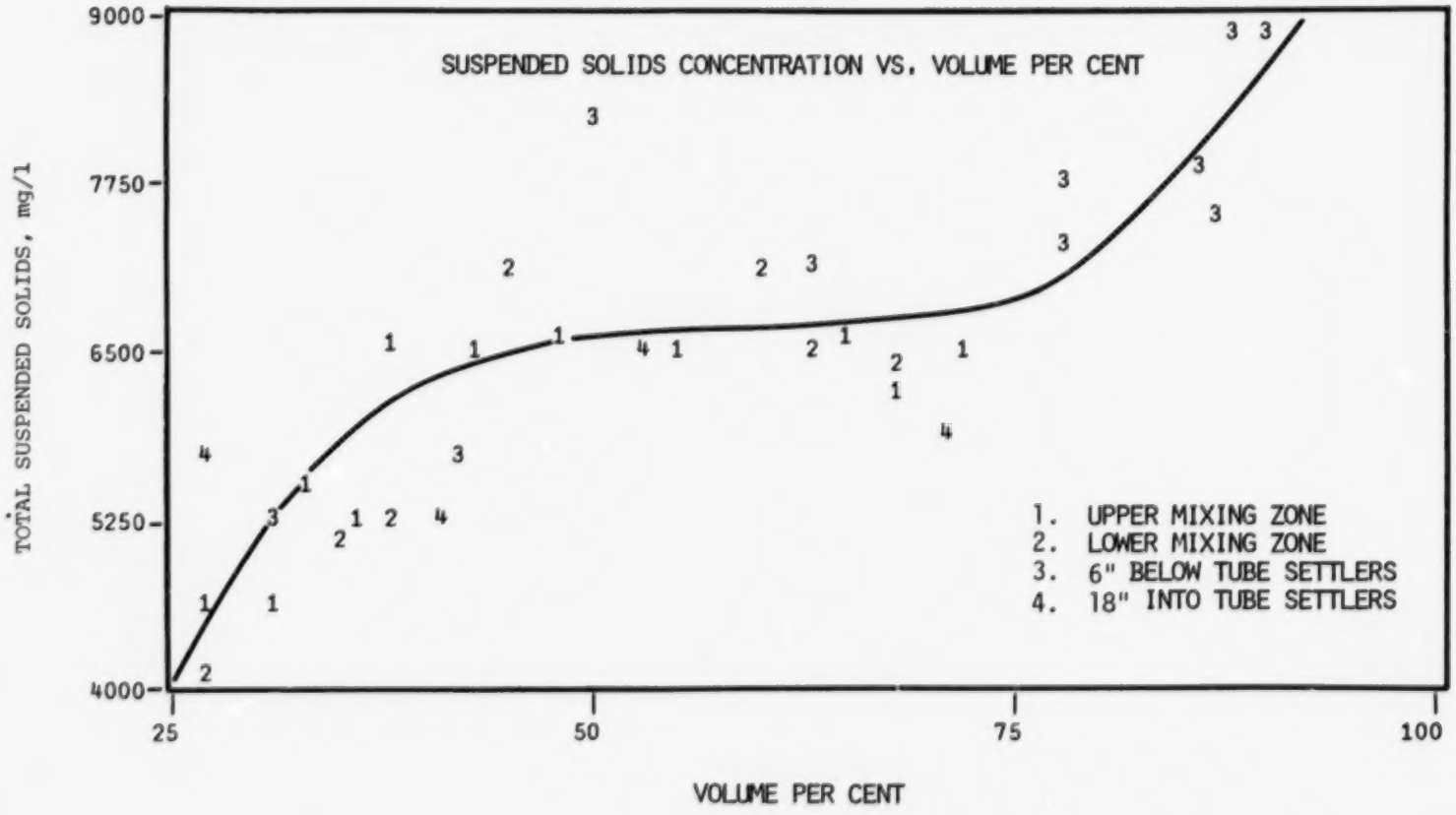

Figure 20. Relationship between blanket solids concentrations measured as mg/l and volume per cent solids.

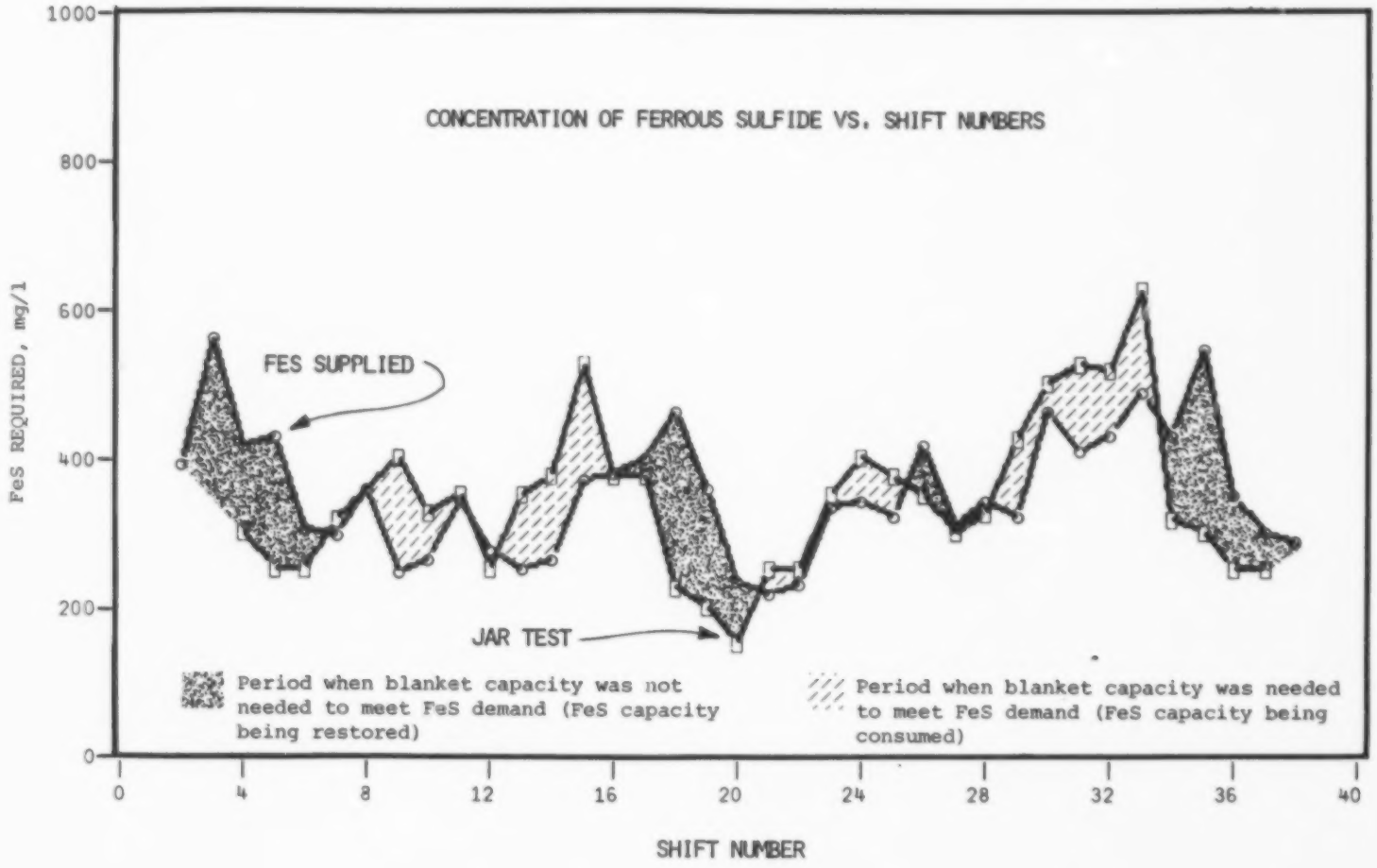

Figure 21. Effect of ferrous sulfide requirement on the reserve sludge blanket capacity as a function of time.

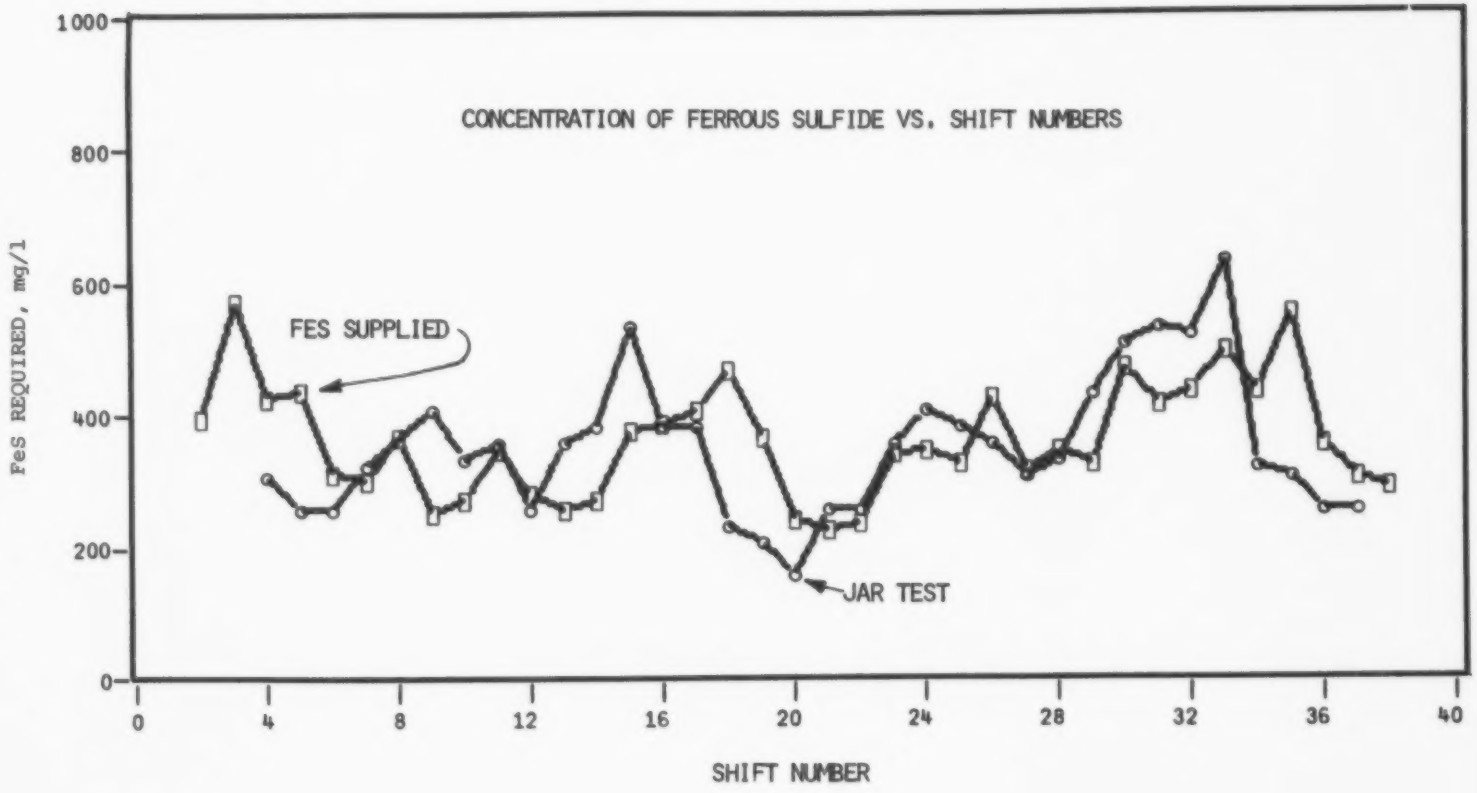

Figure 22. Actual ferrous sulfide supplied compared to jar test requirement as a function of time.

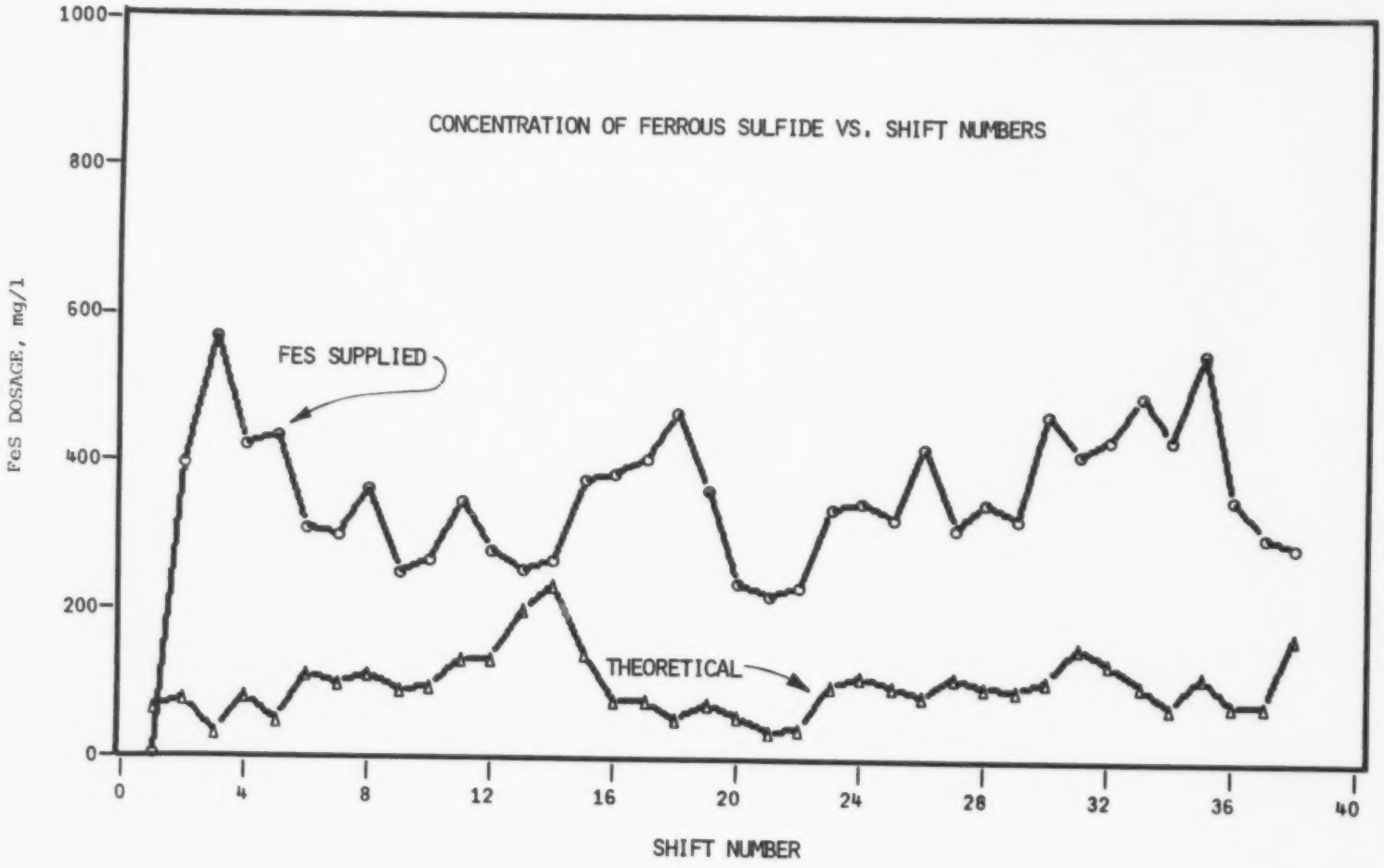

Figure 23. Theoretical ferrous sulfide requirement compared to actual supply as a function of time.

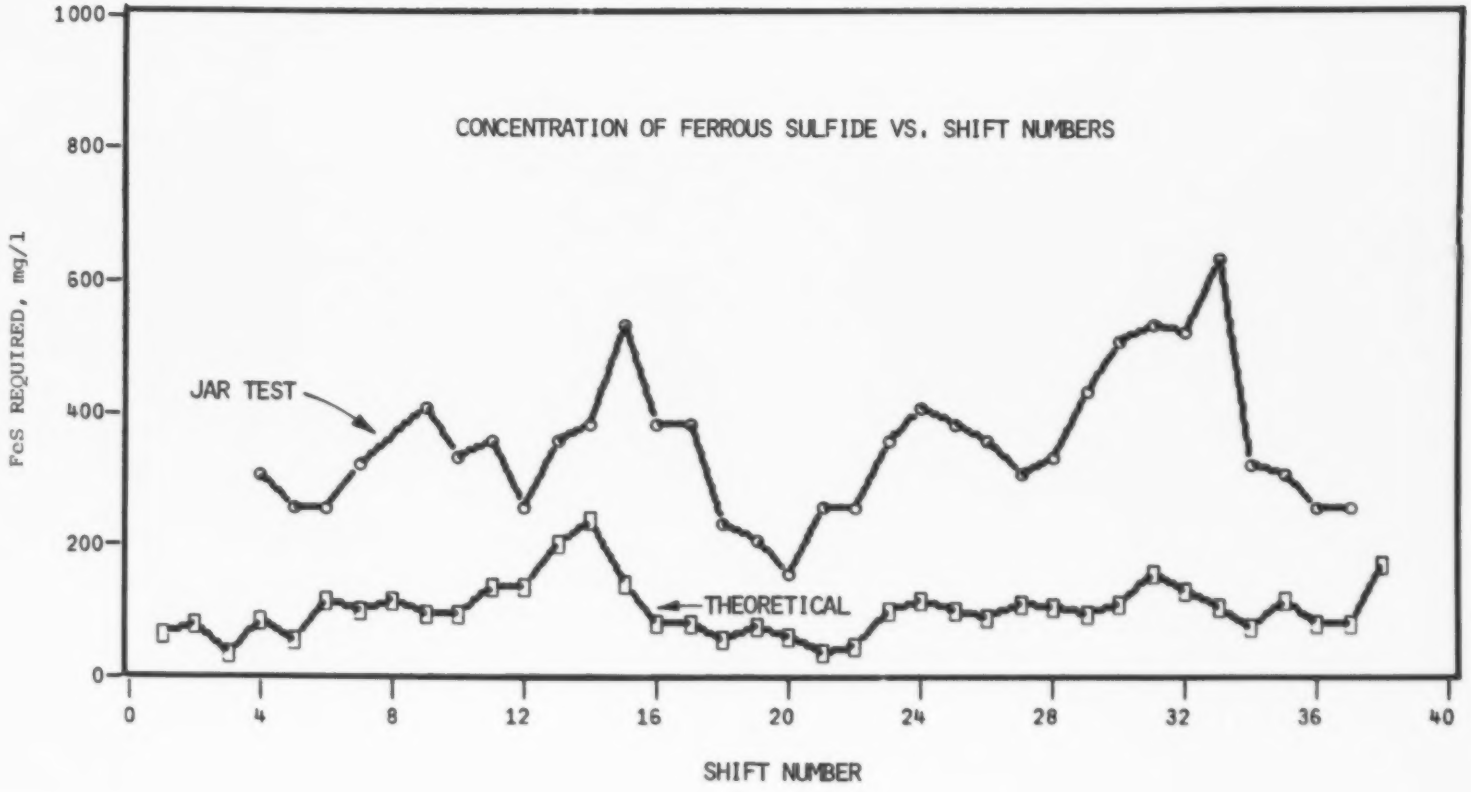

Figure 24. Theoretical ferrous sulfide requirement compared to jar test requirement as a function of time.

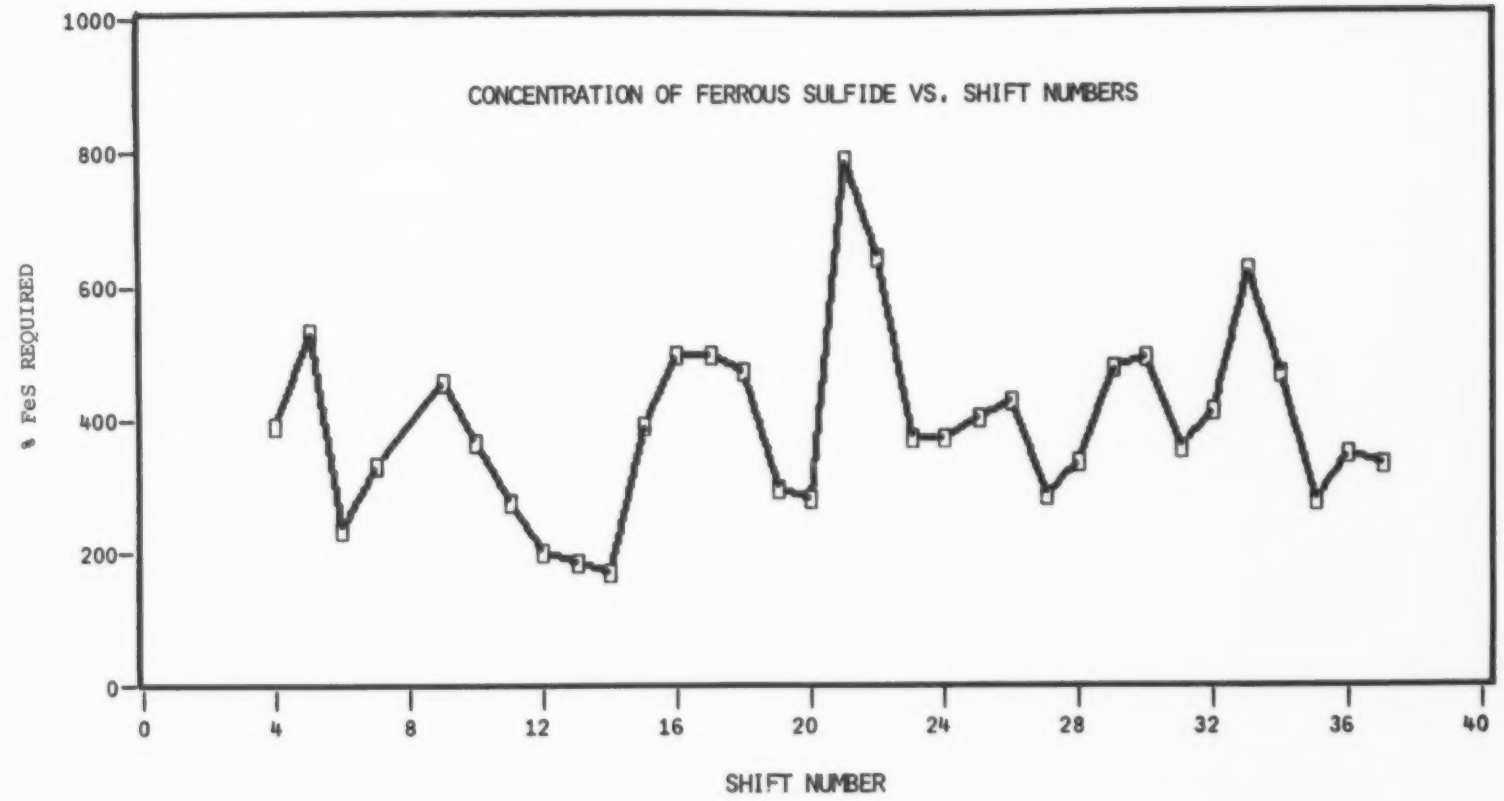

Figure 25. Jar test requirement expressed as percentage of theoretical requirement as a function of time.

EQUIPMENT PERFORMANCE

Precipitator Performance

As discussed in Section 5, the function of the Precipitator is to carry out the chemical reactions, and subsequent separation processes, necessary for removal of heavy metals from the liquid waste.

The wastewater to the Precipitator contained both suspended solids and dissolved metals. The range of suspended solids in the influent to the Precipitator, excluding ferrous sulfide, was 17-396 mg/l. The range of suspended solids in the effluent stream of the Precipitator varied from less than 1 mg/l to 30 mg/l. Figure 26 shows the average total suspended solids concentration in the Precipitator influent and effluent on a shift-by-shift basis. Using the average influent loading of suspended solids and the highest effluent carryover of suspended solids, the Precipitator removed 88% of the influent suspended solids.

In addition to the suspended solids present in the neutralized influent, the ferrous sulfide feed is also considered a suspended solids loading to the Precipitator. When ferrous sulfide is included, the total removal of suspended solids becomes 96%. Figure 27 shows the averaged combined influent suspended solids and ferrous sulfide concentration in the Precipitator influent on a shift-by-shift basis. The city effluent discharge requirement for maximum suspended solids is 1500 mg/l. However, above 300 mg/l suspended solids, a surcharge is imposed.

The required effluent limits and the total metals content of the Precipitator influent and effluent are summarized in Table 8 below. Since the Precipitator effluent contains less than 300 mg/l, the filter has not been required to meet the suspended solids limits. However, to meet the desired effluent metal limitations, a filter is necessary to remove the average 1 to 2 mg/l of combined precipitated metals in the Precipitator suspended solids carryover.

TABLE 8. REMOVAL OF METALS BY PRECIPITATOR

Metal	Avg. in influent mg/l	System guaranteed effluent requirement mg/l	Avg. in Precipitator effluent mg/l
total-Zn	39.5	1.0	0.21
total-Fe	0.52	-	0.92
total-Cu	<0.01	0.2	<0.01
total-Cr	22.3	0.1	0.16

The results of monitoring the Precipitator influent and effluent metal concentrations, by laboratory analyses of grab samples, are shown in Figures 28, 29, and 30 for total-chromium, hexavalent chromium and zinc, respectively.

The metal concentrations in the Precipitator effluent meet all the requirements of the City of Paris, Tennessee with the exception of total-chromium. Therefore, the dual media filter was particularly important in the final removal of this precipitated chromium hydroxide carryover from the Precipitator.

Dual Media Filter Performance

The performance of the filter in removing metals and other suspended solids in the form of carryover from the Precipitator was monitored by analyzing grab samples of the Precipitator effluent and filter effluent. These results are summarized in Table 9 as follows:

TABLE 9. REMOVAL OF METALS AND TSS BY FILTER

Parameter (mg/l)	Range of Precipitator effluent average concentrations (mg/l)	Range of filter effluent average concentrations (mg/l)
total-Zn	0.1 to 0.5	<0.05
total-Fe	0.3 to 4.0	<0.50
total-Cu	<0.01	<0.01
total-Cr	0.1 to 1.0	<0.04
Cr^{+6}	<0.05	<0.04
TSS	1.0 to 10	0.5 to 1.0

It is apparent from these results that most of the suspended material that is removed by the filter is a combination of zinc, iron, and trivalent chromium precipitates.

Filter Press Performance

The design of the sludge dewatering system and the monitoring operation for the filter press are discussed in Sections 4 and 5, respectively. Monitoring of the influent sludge flow and measurement of resulting sludge cake solids concentration were performed periodically to determine the average operating cycle time, capacity, and dewatering performance of the filter press.

The cake produced for most operating cycles was in the range of 23 to 30 percent solids on a weight to weight basis. In a few instances, the cake appeared substantially drier but, in these cases, it happened that the percent solids were not determined.

The average filter press operating rate, established at Holley, was 0.68 m^3/hr (3 gpm). At this flow rate, the press could normally be operated for 10 to 14 hours. Operating cycle time varied with the initial sludge level in the sump, and the sludge blowoff rate to the system. If the sump level was

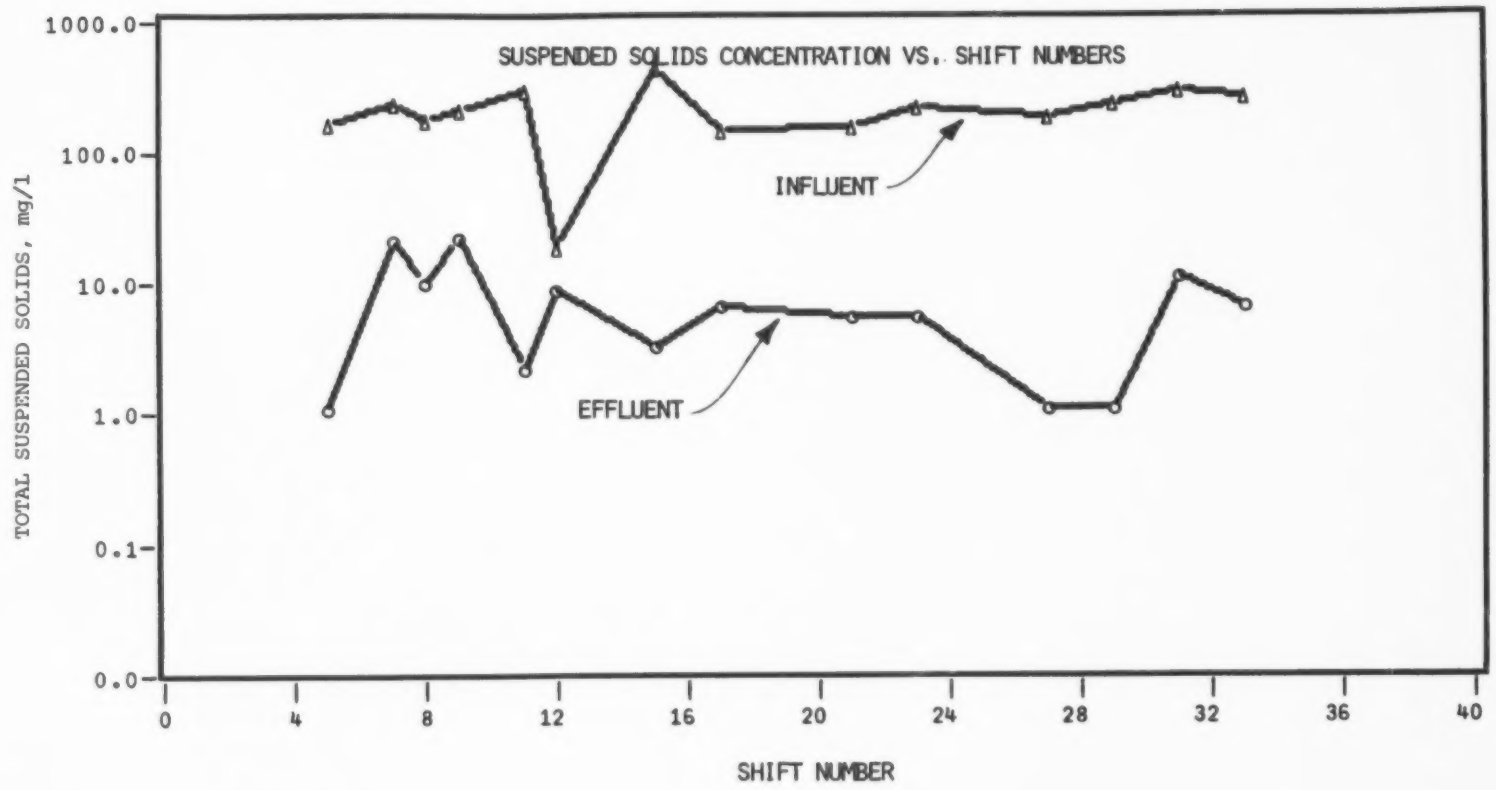

Figure 26. Concentration of total suspended solids in Precipitator influent and effluent as a function of time.

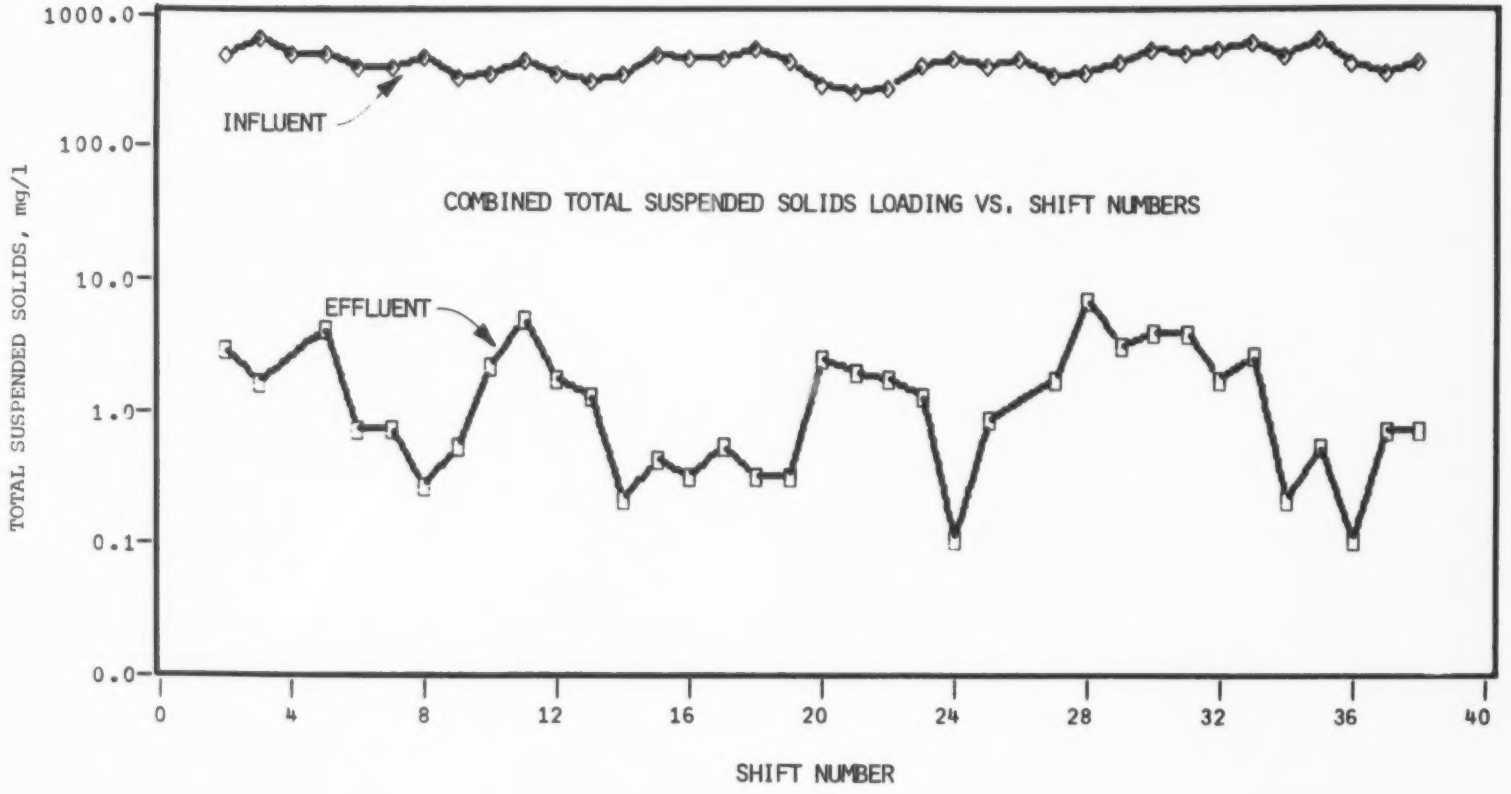

Figure 27. Total Precipitator suspended solids loadings as a function of time.

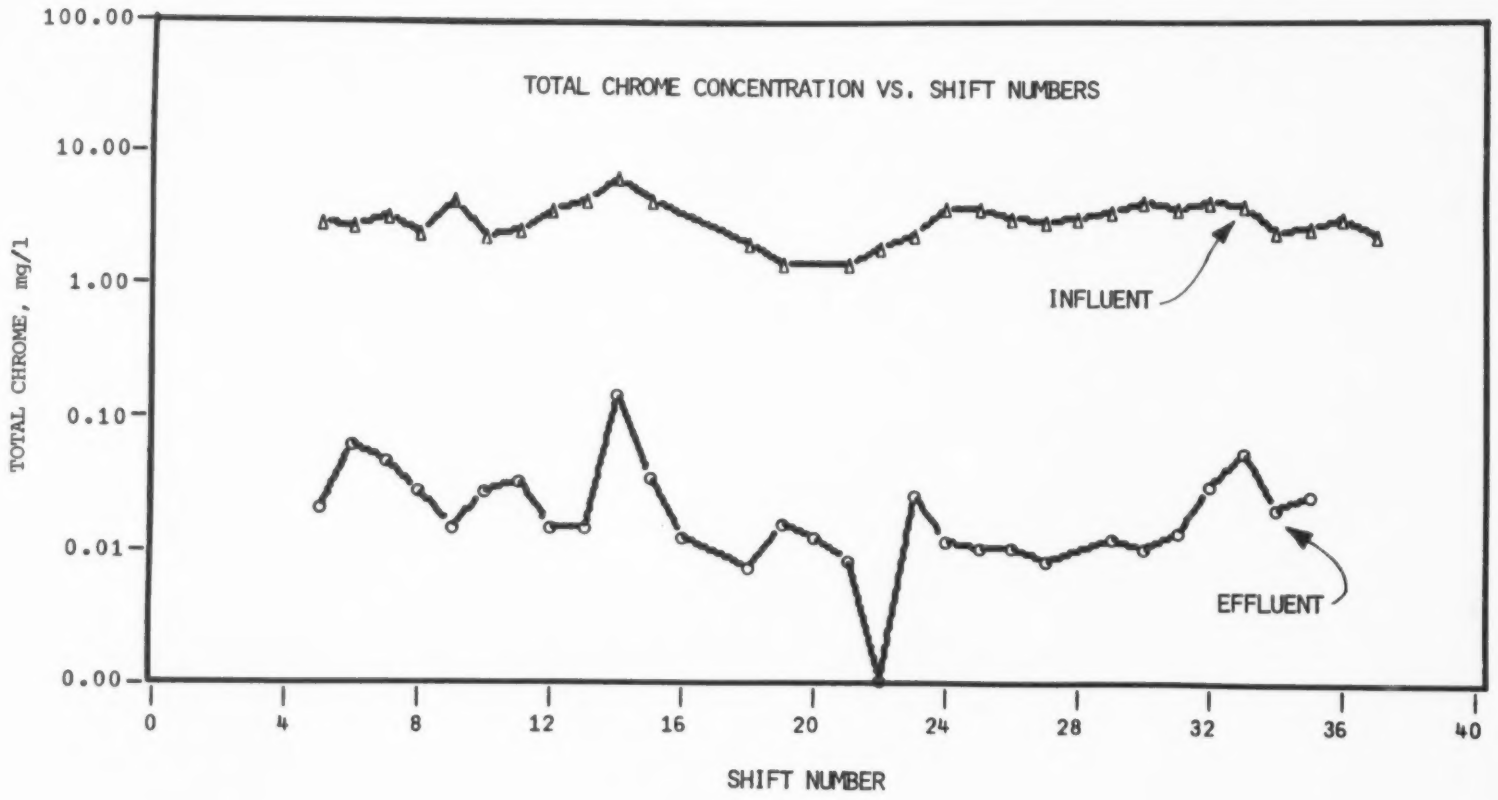

Figure 28. Average concentration of total Cr in Precipitator influent and effluent as a function of time.

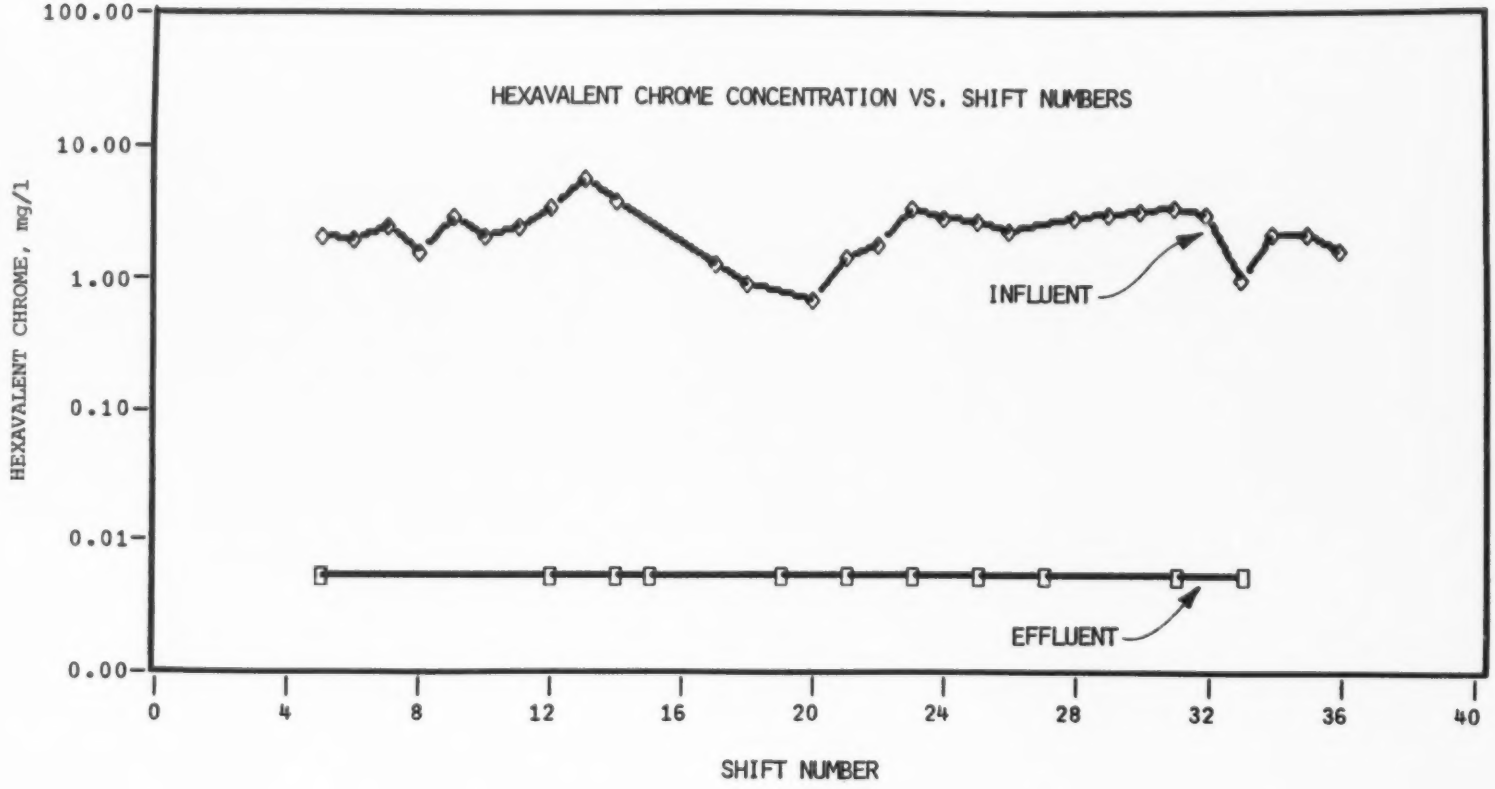

Figure 29. Average concentration of Cr^{+6} in Precipitator influent and effluent as a function of time.

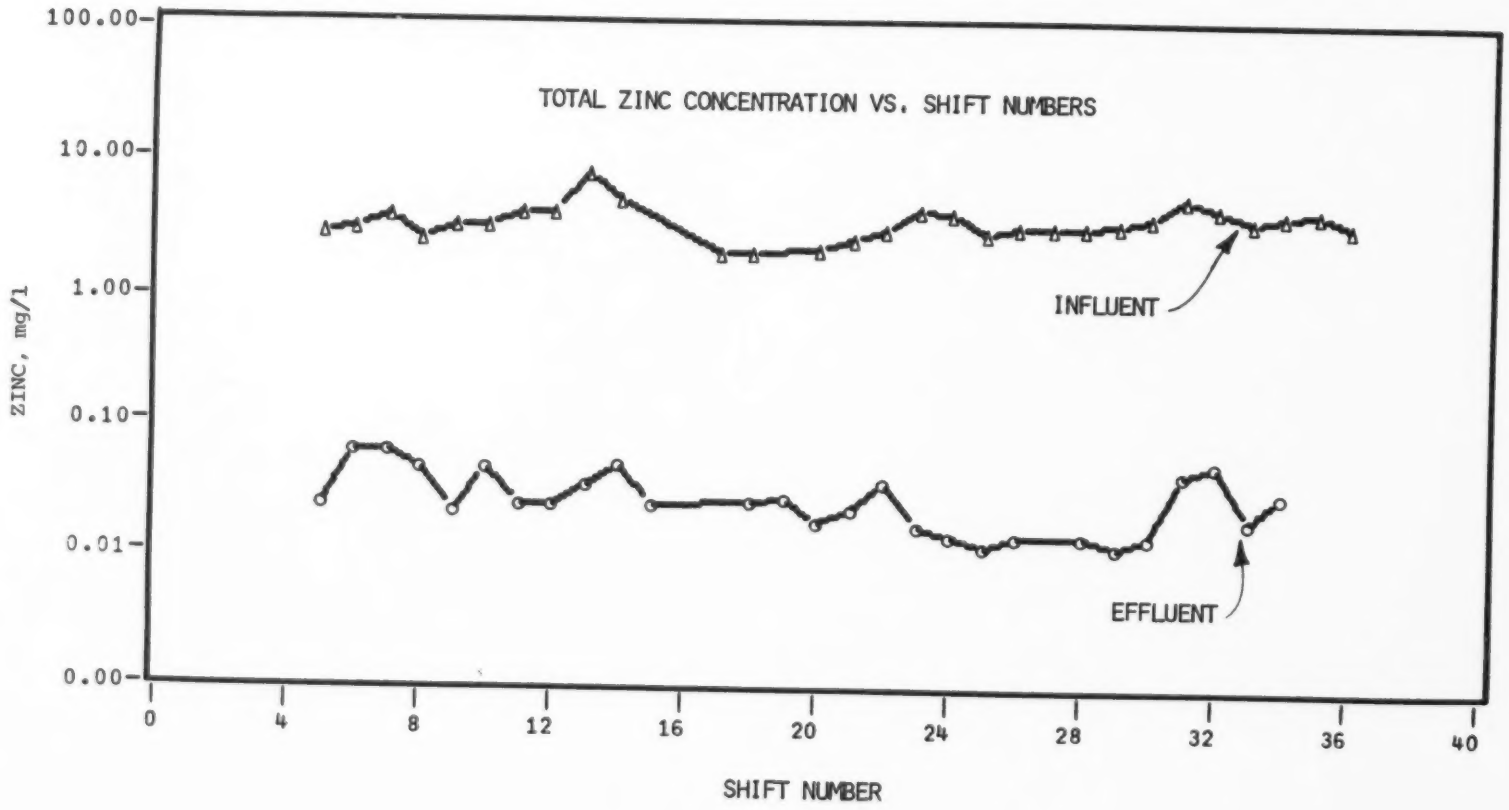

Figure 30. Average concentration of total Zn in Precipitator influent and effluent as a function of time.

high at the start, the operating cycle time would be short because the press would be accumulating solids continuously. If the level was low initially, the press would start recycling filtered water (automatic low level recycle system) and the solids accumulation with time would be correspondingly less.

The filtrate from the press contained between 3 mg/l (beginning of cycle) and 22 mg/l (end of cycle) of suspended solids. Even when using the worst conditions experienced, that of low solids load into the press and high suspended solids breakthrough into the filtrate, the press removed 99.9 percent of the influent suspended solids.

The volume reduction produced by the filter press was 92.5 percent. The original volume of sludge (Precipitator blowoff) was 1.96 cubic meters (69.2 cubic feet) per press operating cycle, while the volume of cake was 0.147 cubic meters (5.2 cubic feet). The solids concentration was therefore increased by a factor of about 13.4 from the original. Figures 31, 32, and 33 show the operating characteristics of the filter press.

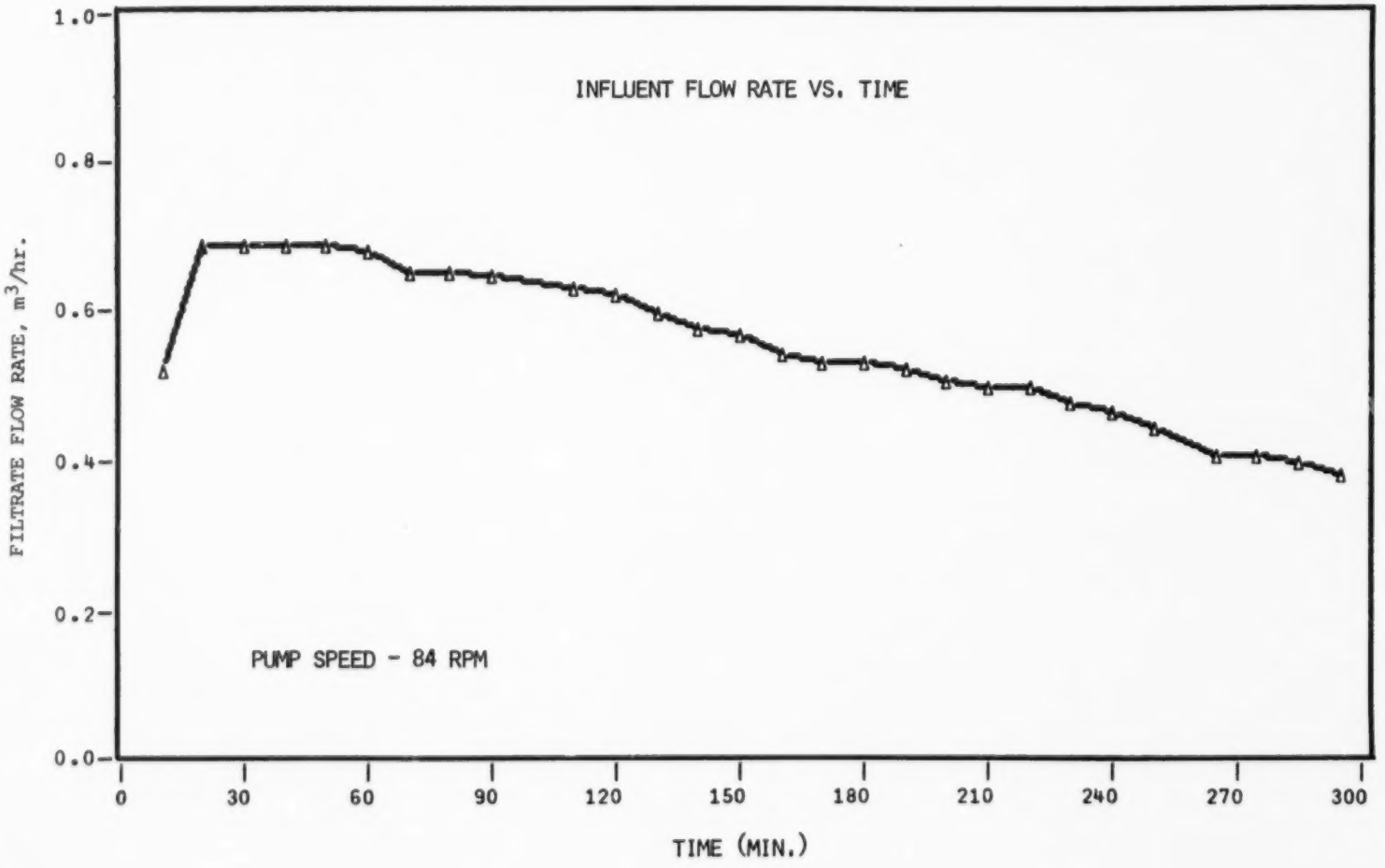

Figure 31. Actual flow rate from filter press as a function of time.

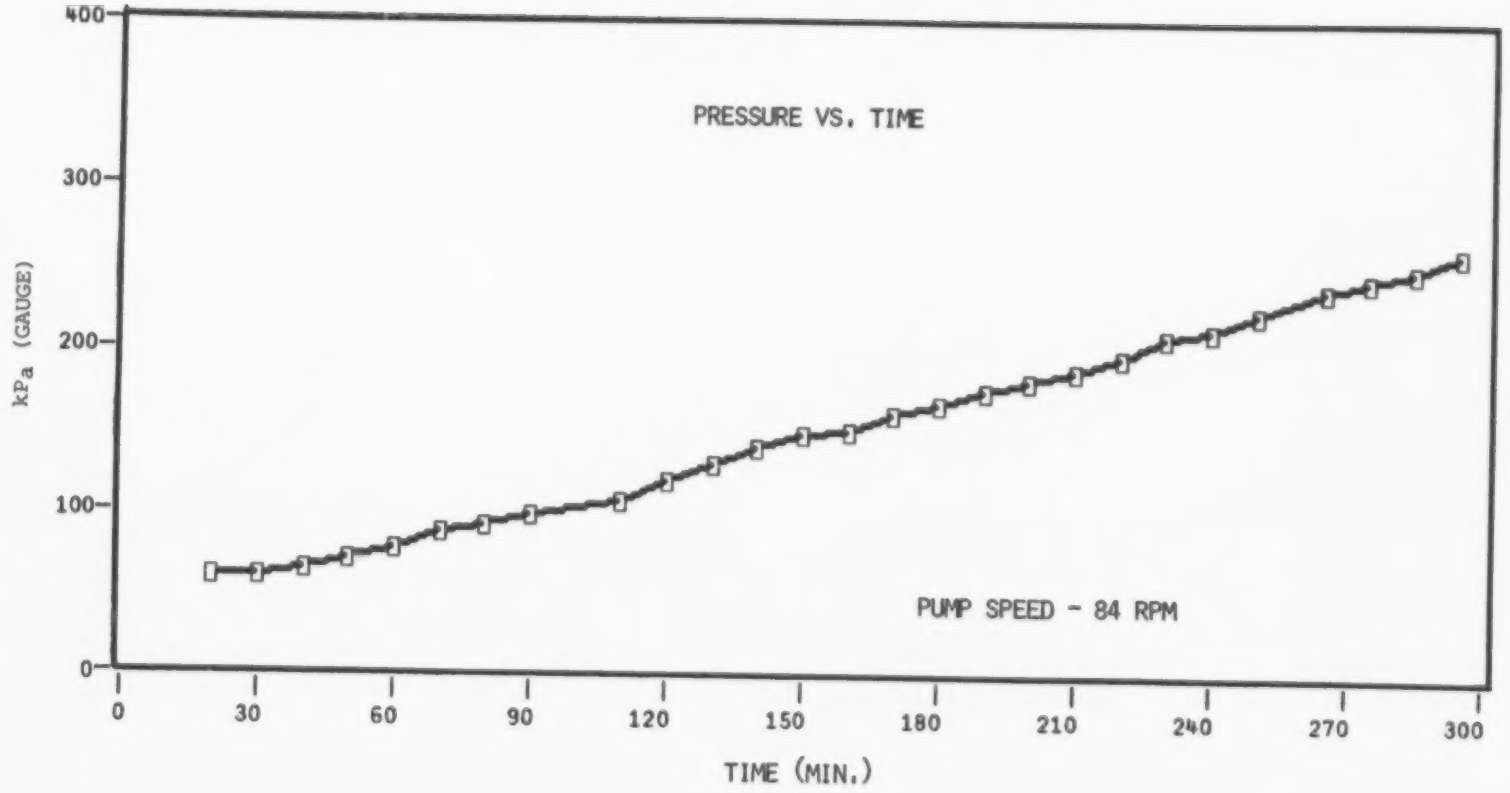

Figure 32. Filter press inlet pressure as a function of time.

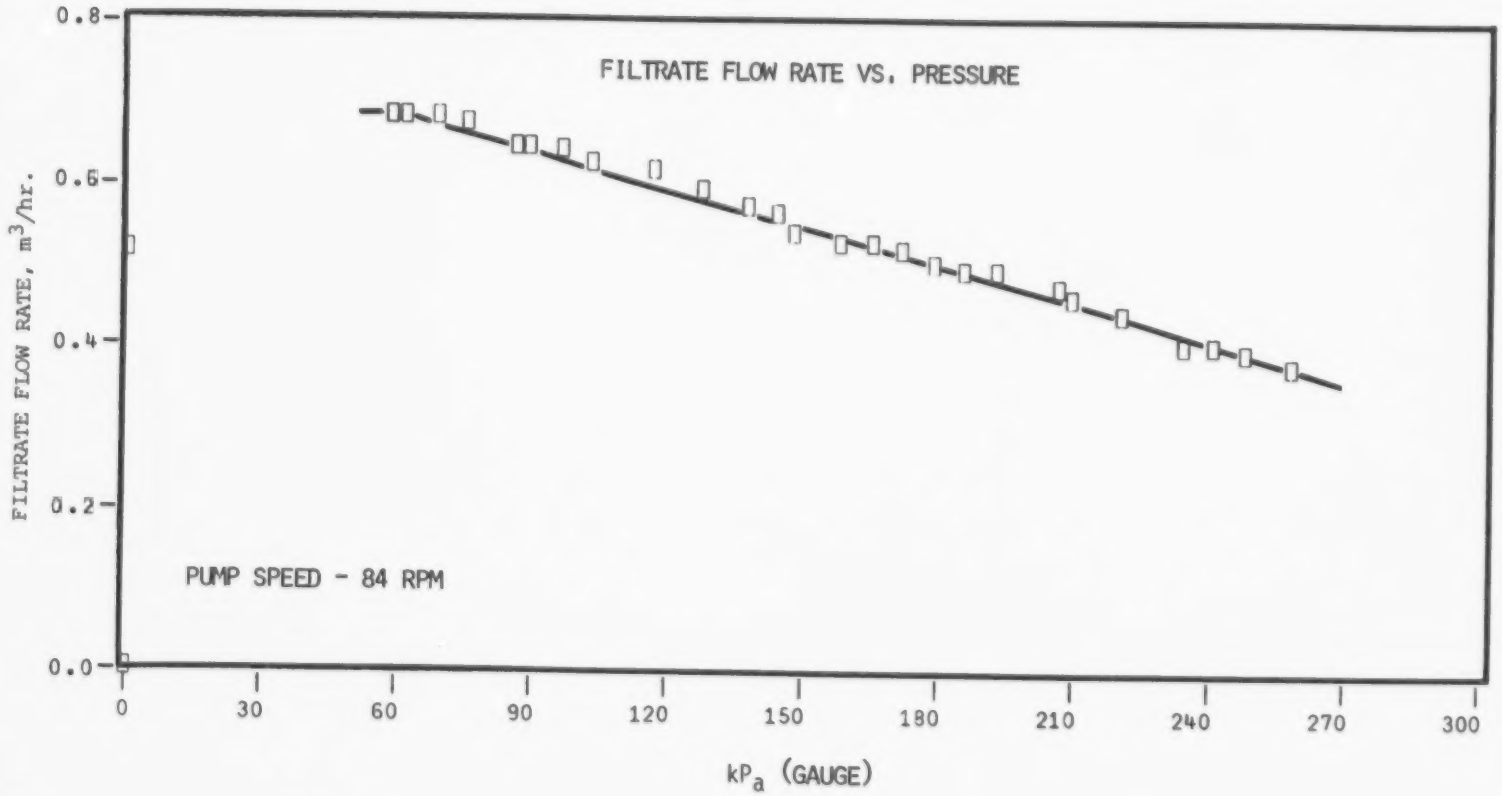

Figure 33. Filter press inlet pressure as a function of inlet flow rate.

SECTION 7

ECONOMIC EVALUATION

GENERAL EVALUATION OF COST EFFECTIVENESS

Evaluating the economics of the Sulfex^{TN} process is an objective of this study. Although a comprehensive economic comparison of Sulfex^{TN} and conventional treatment processes is beyond the scope of the study, factors related to capital and operating costs for conventional treatment are also considered.

Equipment Comparison

The type of equipment needed for the unit operations in Sulfex^{TN} is basically similar to the type required for conventional hydroxide precipitation processes. The main differences between Sulfex^{TN} and conventional systems (with acid-sulfite reduction for Cr^{+6} removal) are in the chemical feeding and controlling equipment.

Sulfex^{TN} Equipment--

Sulfex^{TN} uses a chemical feed system that includes three chemical holding tanks. Two of these tanks have slow speed agitators for preparing and holding ferrous sulfide slurry. Conventional chemical slurry metering pumps are used for transfer of ferrous sulfide to the process. The third tank is used to dissolve ferrous sulfate for use in preparing the ferrous sulfide.

Conventional Treatment Equipment--

Conventional chromium destruction requires a separate step at low pH (i.e. pH 2.0 to 2.5). A corrosion resistant reaction tank with high speed mixing and controllers for pH and oxidation-reduction potential is required. The chemical feed equipment requirements include an acid holding tank and metering pumps as well as a sulfite solution tank and metering system.

The complete installed cost for a 7.9 m^3/hr (35 gpm) treatment system, using either Sulfex^{TN} or conventional technology, is estimated to be roughly the same. This is based on using similar major equipment units. The differences in the chemical feed and controlling equipment could possibly show a trade-off in cost but are likely to be about 50 percent more expensive for the conventional systems.

Operating Cost Comparison

In treating the wastewater at Holley, operator time requirements and chemical costs are the major portions (i.e. about 90 percent) of the operating cost. In both Sulfex^{TN} and conventional treatment technologies, the operating

cost is dependent on the variability of the wastewater composition and the total concentration of heavy metals.

The cost of operating conventional treatment appears to be more dependent on operator attention and maintenance for controlling the chemical reaction processes. The operating cost of Sulfex^{TN} treatment appears to be more highly dependent on the average concentration of heavy metals in the wastewater, especially zinc or other heavy metals that precipitate as sulfides.

The cost of chemically removing Cr^{+6} is estimated to be roughly equivalent, for Holley's wastewater, by Sulfex^{TN} and conventional treatment. Hexavalent chromium is removed as $Cr(OH)_3$, after the reduction reactions, by both treatment technologies.

Operator Attention and Maintenance--

The successful removal of Cr^{+6} is considerably more dependent on the design and accuracy of the chemical feed controlling equipment with conventional systems than it is with Sulfex^{TN}. Rigorous control of chemical feeds for conventional Cr^{+6} reduction requires constant attention and maintenance of the control equipment by the operators. The more variable is the wastewater, the more operator attention is required.

The Sulfex^{TN} feed control is less complicated to operate and maintain than the low pH and oxidation-reduction potential control equipment needed for conventional treatment. Instead, the control of chemical dosages to the Sulfex^{TN} process, to match wastewater metal variations, is optimized by monitoring the feed of ferrous sulfide with simple visual jar tests.

Chemical Costs--

At Holley, the average total chemical cost, per eight-hour shift, is calculated at $17.45 during steady state operation of Sulfex^{TN}. The estimated optimum total chemical cost for conventional treatment at Holley is $11.07/shift. The cost of conventional Cr^{+6} reduction and precipitation alone accounts for $10.70/shift. The remaining $0.37/shift is for the removal of zinc. These costs are based on average wastewater loadings of 1.61 kg/shift Cr^{+6} and 1.63 Kg/shift Zn in 5.9 m^3/hour flow at pH 5.2 to 6.5.

On a theoretical basis, the total chemical cost for Sulfex^{TN}, including lime, polymer and ferrous sulfide, would be $8.04/shift. The cost of the theoretical (stoichiometric) ferrous sulfide requirement would be $5.28/shift. The average actual ferrous sulfide usage (at $14.69/shift) is about 2.8 times stoichiometric. If both metals require the same excess above stoichiometric ferrous sulfide dosage, the Cr^{+6} requirement is about $8.23/shift and the Zn requirement about $6.50/shift. Therefore, the cost of Zn removal is a major part of the chemical cost in Sulfex^{TN} treatment but would be only a minor cost in conventional treatment.

It appears Sulfex^{TN} economics become more favorable as the concentration of Zn in the wastewater diminishes relative to the Cr^{+6} concentration. For example, assume the Cr^{+6} loading remains at 1.61 kg/shift, but the Zn loading is reduced by 90 to 95 percent (i.e. from 1.63 kg/shift to about 0.08-0.16 kg/shift). Assuming a reduction in ferrous sulfide and polymer can be made that

is stoichiometrically equal to 2.8 times the difference in Zn loading, the total cost of Sulfex^{TN} can be reduced to about the $10.71 to $11.07/shift range. This is essentially equal to the estimated cost for conventional treatment.

Therefore, from an economic standpoint, it appears justifiable to separate, in a preliminary settling step, the 90 to 95 percent of the Zn that precipitates, as $Zn(OH)_2$, in the neutralization step. Then, the greater heavy metal removal reliability of Sulfex^{TN} can be applied at about the same total operating cost as conventional hydroxide treatment.

The reliability of conventional technology is reflected in the State of Tennessee's guidelines which are shown in Table 1 of this report. The reliability of Sulfex^{TN} technology is summarized in Table 7 as demonstrated by this study.

YEARLY OPERATING COSTS FOR SULFEX^{TN} AT HOLLEY

The yearly operating cost, excluding depreciation and licensing fees, for the treatment system at Holley Carburetor is outlined below. This cost results from charges incurred by operators, utilities, and chemicals.

The estimated yearly operating cost, based on plant performance to date, is as follows:

1. Operators Salaries:

$10,800 per operator x 2 operators	=	$21,600
+ fringe benefits at 40%	=	8,640
Total Salaries	=	$30,240/year

2. Electricity:

$$203.32 \frac{\text{kwh}}{\text{day}} \times \frac{5 \text{ day}}{\text{wk}} \times \frac{52 \text{ wk}}{\text{yr}} \times \frac{\$0.0191}{\text{kwh}} = \$1010/\text{year}$$

3. Water:

$$4162 \text{ m}^3 \times \$0.053/\text{m}^3 = \$220/\text{year}$$

4. Chemicals:

$$\frac{\$17.45}{\text{shift}} \times \frac{2 \text{ shifts}}{\text{day}} \times \frac{260 \text{ day}}{\text{yr}} = \$9074/\text{year}$$

5. Sludge Handling and Disposal Cost:

$$\frac{\$15}{\text{day}} \times \frac{260 \text{ days}}{\text{yr}} = \$3900/\text{year}$$

Total Operating Cost is therefore:

Salaries		$ 30,240
+ Electricity	=	1,010
+ Water	=	220
+ Chemicals	=	9,074
+ Sludge Disposal	=	3,900
TOTAL	=	$ 44,444/year

For this installation, it is seen that the operator's salaries account for 68% of the yearly operating cost. In other cases, however, two full-time operators may not be required. The utility costs are estimated from actual figures obtained at the operation.

Figure 34 shows the total chemical costs per shift actually observed during this study. Figures 35, 36, 37, 38, and 39 show costs per shift for the individual chemicals.

Chemical cost has been determined by averaging the total chemical usage over the last 16 shifts using the delivered chemical price. The first 22 shifts were eliminated from this cost estimate. During this first period, the operation of the system was not yet at steady state conditions and is considered not representative of normal operating conditions. Data which was collected prior to the 23rd shift represents unstable operation due to normal trial and error of start-up and operator training.

It is assumed that the real chemical requirement can be reduced from the observed $17.45 per shift by at least 10%. This assumption is based on the existing evidence that shows the results of jar tests for ferrous sulfide demand, without use of sludge recirculation, are in excess of the real requirement by at least 10%. The supply of ferrous sulfide to this system was controlled by such jar tests during this study.

SULFEX^{TN} CHEMICAL COSTS AT HOLLEY

Delivered Chemical Prices

In preparing ferrous sulfide slurry for this process, ferrous sulfate, sodium sulfhydrate, and hydrated lime are used. Lime is also used for the wastewater neutralization steps. A cationic guar type polyelectrolyte is used to improve coagulation and sedimentation of all precipitated metals and other suspended solids that result during the treatment process.

Per Unit Weight of Chemical Basis--

The following are actual prices paid for chemical delivered to Holley Carburetor Company, Paris, Tennessee:

Ferrous Sulfate, $FeSO_4 \cdot 7H_2O$, granular, 22.7 kg (50 lb) bags = $0.149/kg (6.75¢/lb)

Sodium Sulfhydrate, NaHS, 70/72% flake, 181.4 kg (400 lb) drums = $0.584/kg (26.5¢/lb)

Hydrated Lime, 93%, $Ca(OH)_2$, 22.7 kg (50 lb) bags = $0.1025/kg (4.65¢/lb)

Polyelectrolyte, cationic guar, 45.4 kg (100 lb) drums = $2.32/kg (105¢/lb)

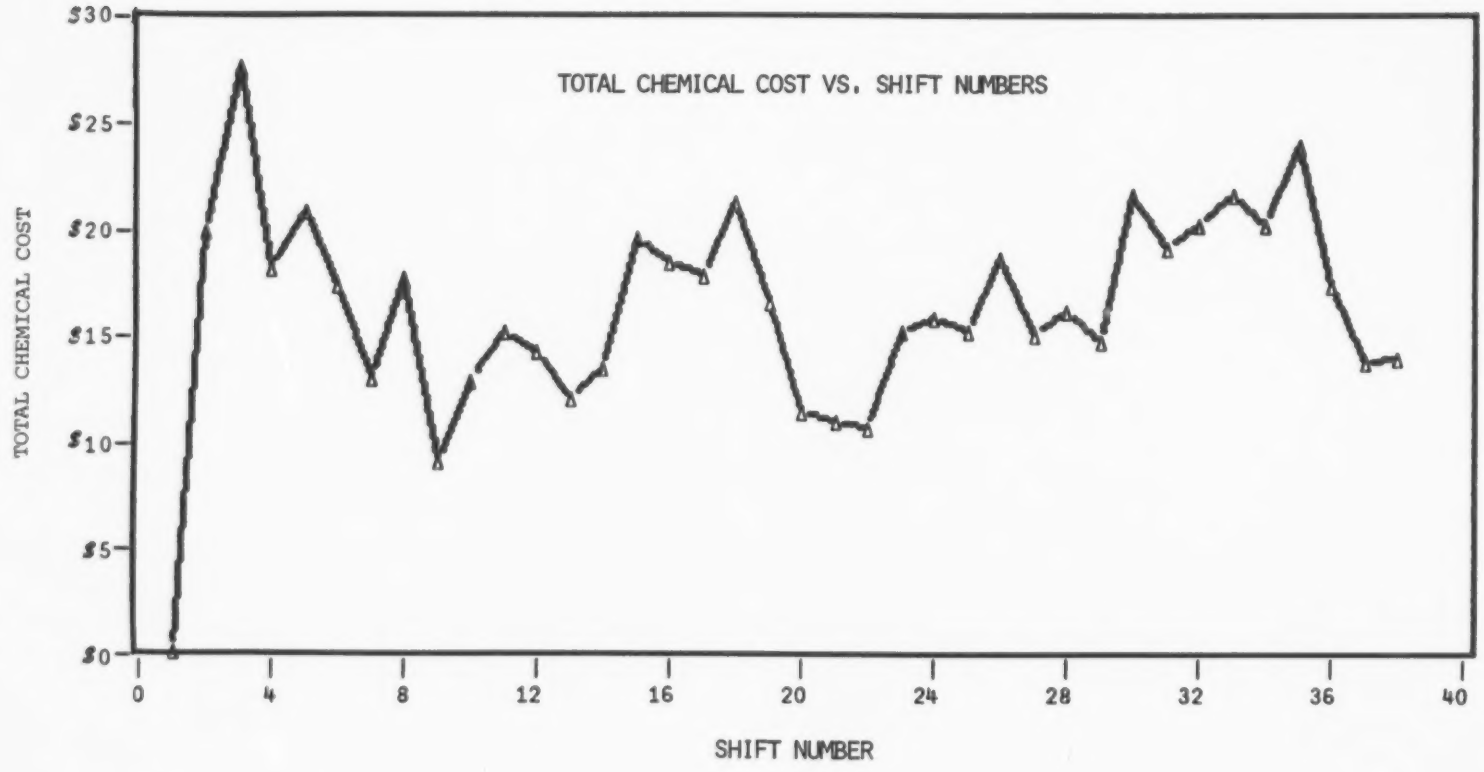

Figure 34. Total chemical cost as a function of time.

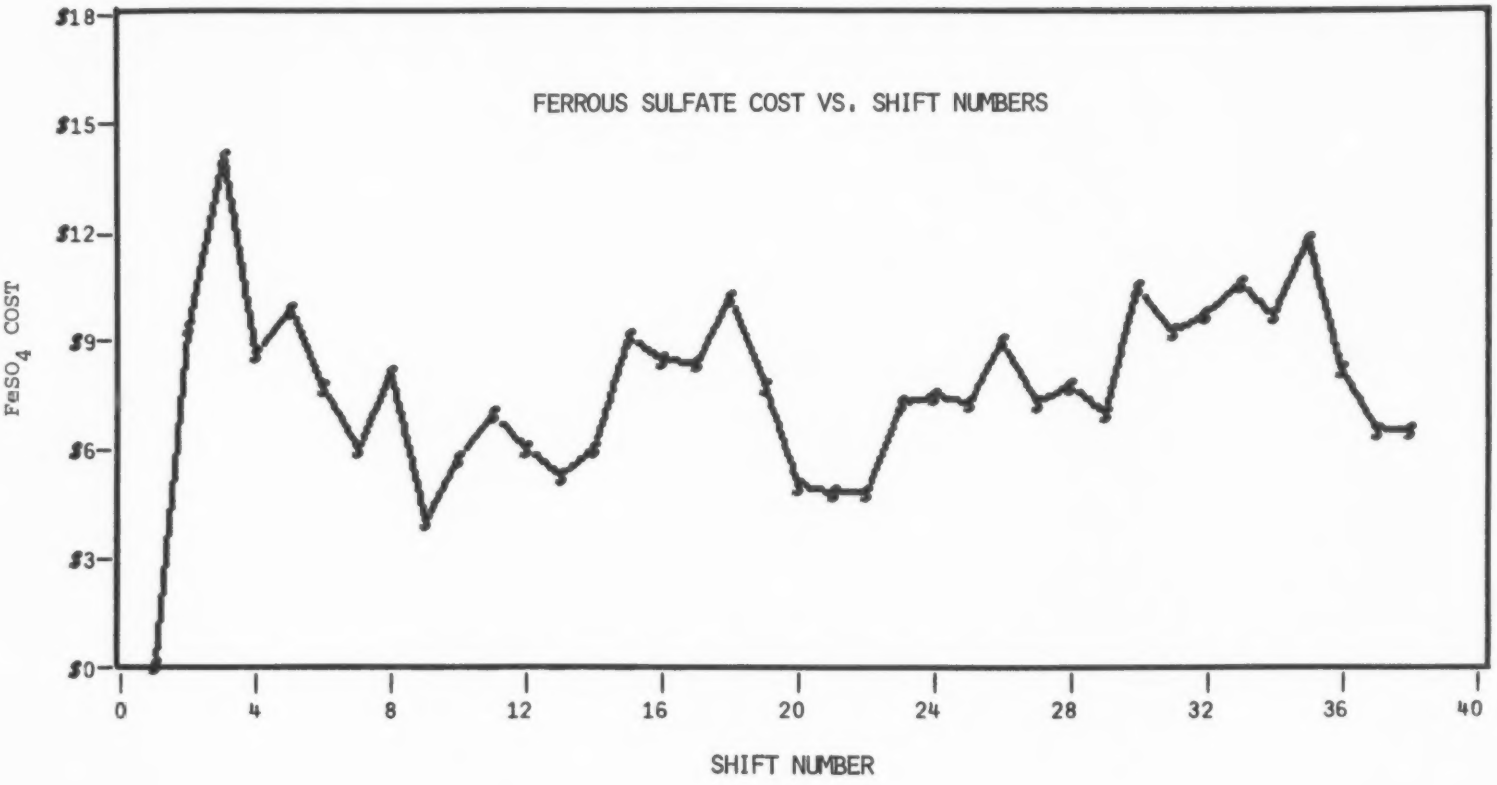

Figure 35. Chemical cost of ferrous sulfate as a function of time.

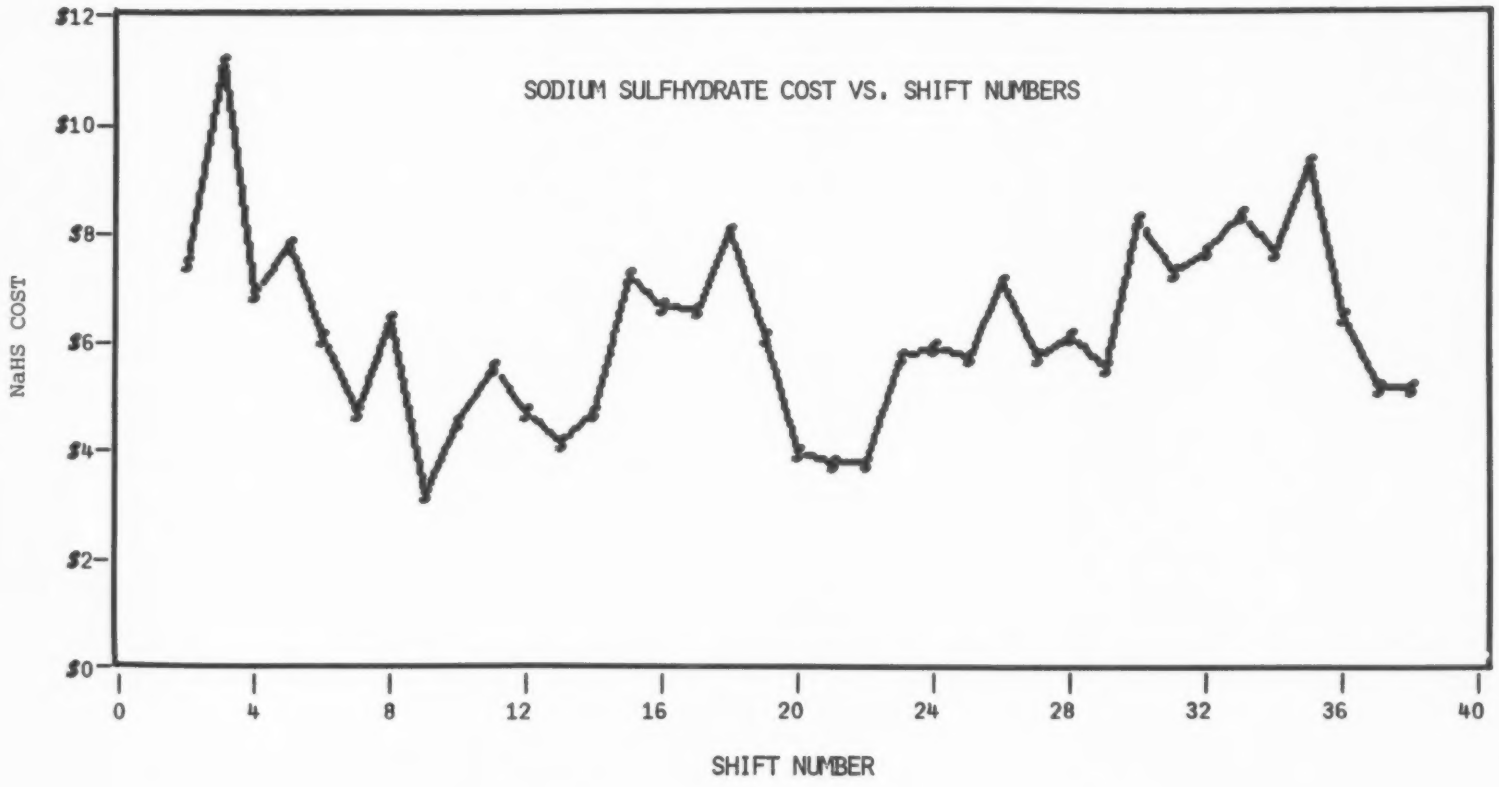

Figure 36. Chemical cost of sodium sulfhydrate as a function of time.

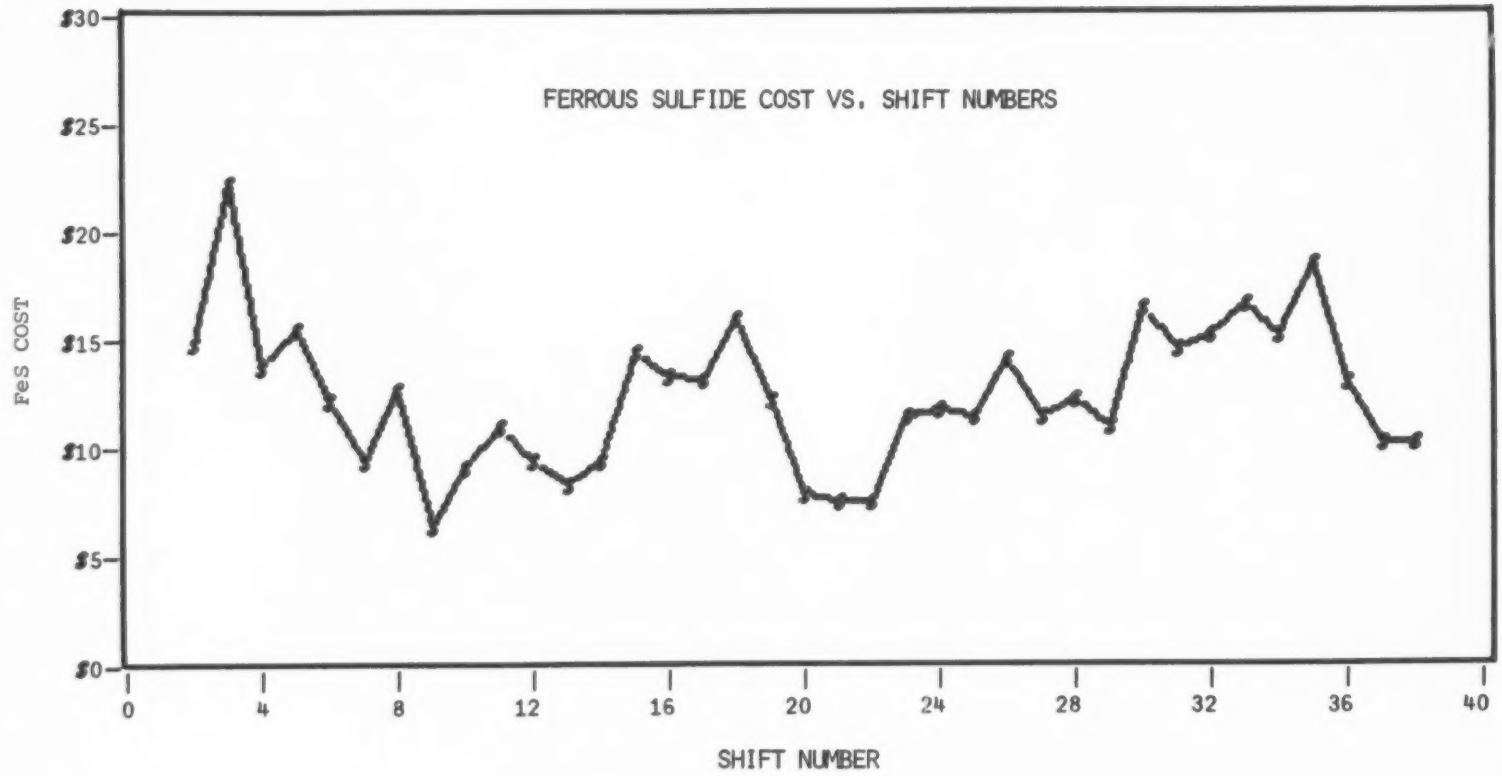

Figure 37. Cost of ferrous sulfide as a function of time.

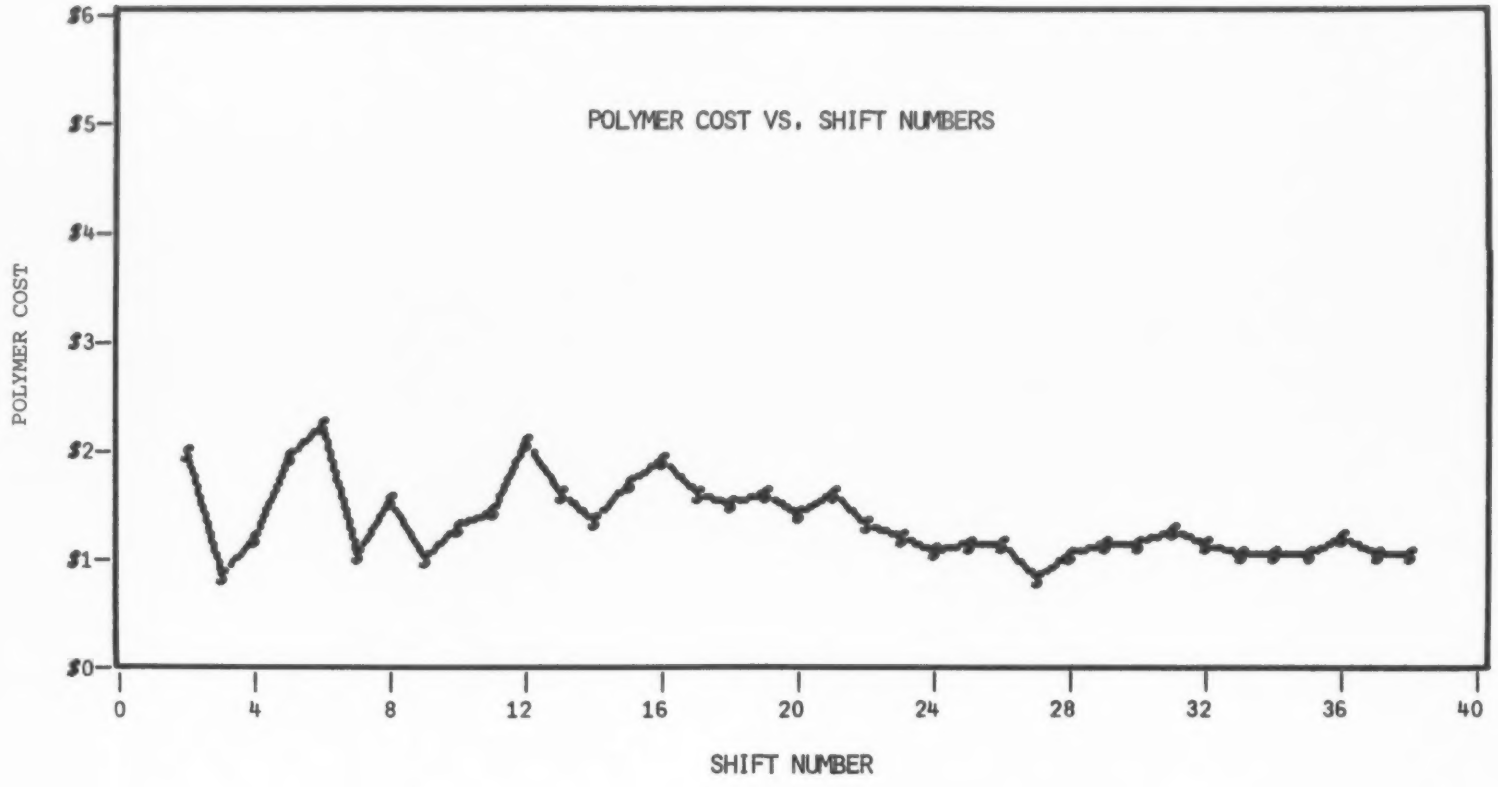

Figure 38. Cost of polyelectrolyte as a function of time.

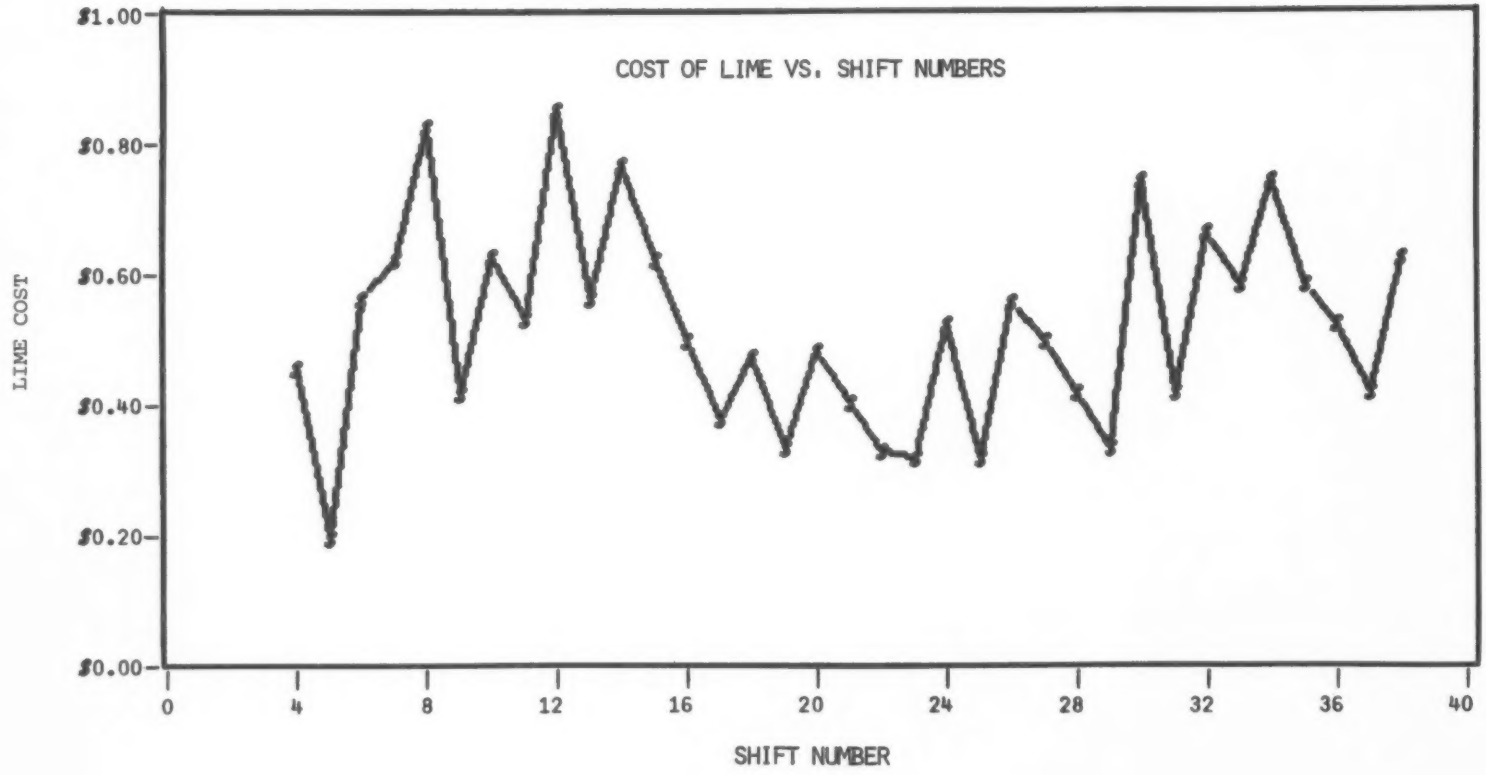

Figure 39. Cost of lime for neutralization as a function of time.

Per Unit Weight of Sulfur Basis--

The quantities of ferrous sulfate, sodium sulfhydrate, and hydrated lime required for each kilogram (2.2 lbs) of ferrous sulfide prepared are as follows: 3.16 kg (6.95 lbs) $FeSO_4 \cdot 7H_2O$, 0.90 kg (1.98 lbs) 71% NaHS, and 0.84 kg (1.85 lbs) 93% $Ca(OH)_2$. Since 2.74 kg (6.03 lbs) of ferrous sulfide is equivalent to 1.0 kg (2.2 lbs) of sulfur, S, the chemical costs, as based on the weight of S supplied, are as follows:

$FeSO_4 \cdot 7H_2O$	=	\$1.29/kg S (\$0.59/lb S)
71% NaHS	=	\$1.44/kg S (\$0.65/lb S)
93% $Ca(OH)_2$	=	\$0.24/kg S (\$0.11/lb S)
Total for FeS	=	\$2.97/kg S (\$1.35/lb S)

The cost of Sulfex^{TN} may be more readily compared with the chemical cost of other sulfide precipitation processes by using the cost per kg of sulfur factor. In these cases, the S is present as ionizable "sulfide" ($S^=$), such as exists in sodium sulfide, Na_2S, or hydrogen sulfide, H_2S.

However, in most conventional hydroxide precipitation systems, sulfide compounds are not used to either precipitate metals or to reduce hexavalent chromium. Conventional chemical reducing compounds usually contain sulfur in the "sulfite" ($SO_3^=$) or "bisulfite" (HSO_3^-) forms, for example. In such cases, the sulfur cannot precipitate a heavy metal sulfide, but it is reactive in reducing Cr^{+6} to Cr^{+3}. These reducing reactions are usually only practical under acidic conditions. The Cr^{+3}, after neutralization with alkali, then precipitates as chromic hydroxide at pH 8.0 to 9.0, as it also does in Sulfex^{TN} treatment.

A more practical basis for cost comparison between Sulfex^{TN} and conventional heavy metal removal is to use cost per unit weight of heavy metal removed. The chemical cost of Sulfex^{TN} and estimated conventional treatment costs, on this wastewater, are assessed in the discussions that follow.

Cost per Kilogram of Metal Removed by "Sulfex"^{TN}

Figure 40 shows the total chemical cost per kilogram of hexavalent chromium and zinc treated. The average total chemical cost per kg of combined Cr^{+6} and Zn treated, based on the final 16 shifts of demonstration = \$5.38/kg. The average cost for ferrous sulfide removal of combined Cr^{+6} and Zn is \$4.53/kg. If we estimate that the real chemical requirement is only 90% of the actual usage (due to the FeS excess dictated by jar tests), the cost of combined Cr^{+6} and Zn removal is reduced to \$4.92/kg.

The individual per kg costs for removing Cr^{+6} and Zn are not easily predicted from existing data. The precipitation of Zn and the reduction of Cr^{+6} to Cr^{+3}, by sulfide, are competing reactions. Completion of one reaction may be favored over the other, depending on existing chemical conditions.

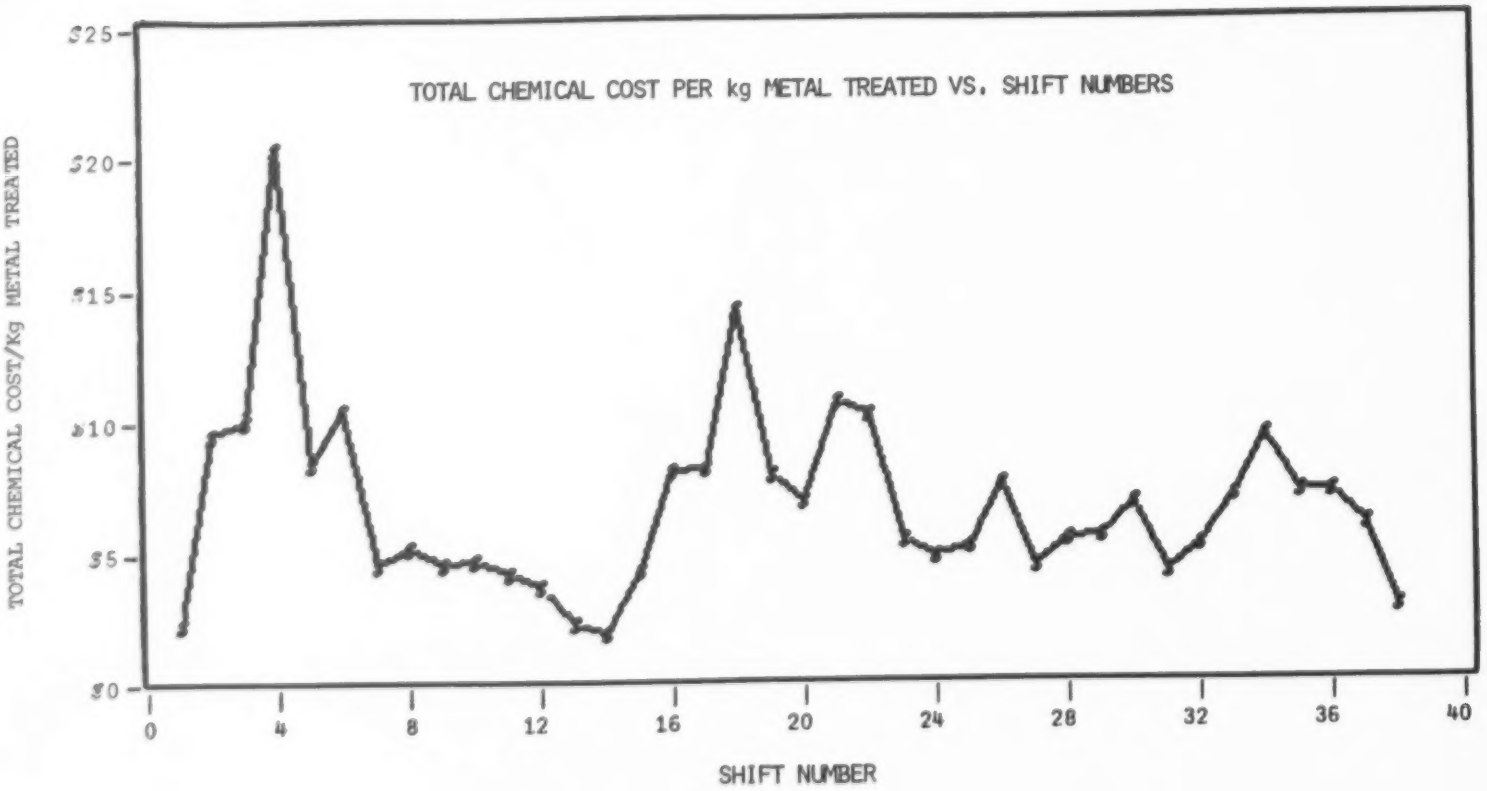

Figure 40. Total chemical cost per kilogram of metal treated as a function of time.

An excess of ferrous sulfide, or any other precipitant (such as hydroxyl ion), is necessary to "drive" each reaction to completion, for the successful removal of each metal. For a general estimate of total ferrous sulfide dosage, it is normally found that the amount of excess required is about one to three times the stoichiometric requirement for the combined heavy metal content of the wastewater. Therefore, in general cases, it may be estimated that each heavy metal present requires about the same ratio of excess ferrous sulfide above its stoichiometric dosage.

At Holley, however, it is known that certain proprietary complexing and chelating agents are present. These materials can affect the reactivity of individual heavy metals in significantly different ways so that a different ratio of excess ferrous sulfide may be required to remove each metal. The solubility of the Zn^{++} cation is, for example, much more strongly influenced by the presence of an anionic complexing legand than is the anionic CrO_4^{-} ion.

Therefore, in this study, the actual chemical costs for Zn and Cr^{+6} individually are not determined. However, it may be assumed that, under all conditions present in this study, the actual ferrous sulfide required by each metal is at least equal to or greater than its stoichiometric requirement.

ESTIMATED COSTS FOR CONVENTIONAL TREATMENT AT HOLLEY

Conventional treatment selected for this estimate consists of acidification of raw waste water with sulfuric acid to pH 2.0. Then, reduction of hexavalent chromium with sodium bisulfite (i.e. $NaHSO_3$) is performed. Next, precipitation of zinc and trivalent chromium is brought about by addition of lime to obtain pH 8.0-9.0.

Delivered Chemical Prices

Per Unit Weight of Chemical Basis--

The costs used in the following estimates are based on prices quoted for delivery to Paris, Tennessee on a quantity basis consistent with the quantities required for treatment under the average wastewater conditions.

The chemical prices are:

Sodium Bisulfite, $NaHSO_3$, 22.7 kg (50 lb) bags = $0.5072/kg (23¢/lb)

Sulfuric acid, 66° Be' H_2SO_4, 181.4 kg (400 lb) drums = $0.1025 kg (4.65¢/lb)

Hydrated lime, $Ca(OH)_2$, 22.7 kg (50 lb) bags = $0.1025/kg (4.65¢/lb)

Polyelectrolyte, anionic polyacrylamide, 22.7 kg (50 lb) bags = $4.96/kg (225¢/lb)

Per Unit Weight of Sulfur Basis--

In conventional reduction of Cr^{+6} to Cr^{+3}, sodium bisulfite ($NaHSO_3$) and sulfuric acid (H_2SO_4) are a commonly used chemical system. Besides $NaHSO_3$, similar partially oxygenated sulfur compounds useful for reducing Cr^{+6} are: metabisulfite ($S_2O_5^{-}$), sulfite (SO_3^{-}), and sulfur dioxide (SO_2).

The theoretical molar ratio of sulfur required for reduction of Cr^{+6}, using any of these conventional agents is 3 to 2, as S to Cr, respectively. Since the delivered prices of these chemicals may vary considerably depending on geography, availability, purity, etc., it is useful to show the price of these reducing agents based on the per unit weight of S supplied.

On a per kg of S basis, the price for sodium bisulfite and sulfuric acid for delivery to Paris, Tennessee are:

$NaHSO_3$ = \$1.64/kg S (\$0.75/lb S)

H_2SO_4 = \$0.15/kg S (\$0.007/lb S)

Total for system = \$1.79/kg S (\$0.82/lb S)

The dosage of H_2SO_4, as based on the theoretical requirement of 0.5 moles of H_2SO_4 per mole of $NaHSO_3$, is calculated at 1.49 kg H_2SO_4/kg S as follows:

$$\frac{0.5 \text{ moles } H_2SO_4}{\text{mole } NaHSO_3} = \frac{48}{104} = 0.46 \text{ kg } H_2SO_4/\text{kg } NaHSO_3$$

$$1 \text{ kg S} = \frac{104}{32.1} \times \text{Kg } NaHSO_3 = 3.24 \text{ kg } NaHSO_3$$

$$3.24 \text{ kg } NaHSO_3 \times 0.46 = 1.49 \text{ Kg } H_2SO_4/\text{kg S}$$

These prices can't be compared directly to Sulfex^{TN} since significant quantities of acid, for controlling the pH at 2.5 or lower during the reduction step, must be considered. Additionally, lime has to be included in the conventional process cost for increasing the pH from about 2.5 up to about 8.0 to 9.0. The lime required to react with this acidity is also quite significant. A more appropriate method of comparison between Sulfex^{TN} and conventional hydroxide precipitation is using the cost per total weight of combined heavy metals removed as the basis.

Cost per Kilogram of Metal Removed by Conventional Treatment

Chemical Requirements for Conventional Cr^{+6} Treatment--

The average wastewater conditions (as used in the estimate for "Sulfex"^{TN} cost), taken over the last 16 shifts of the demonstration, were 5.9 m^3/hour flow (26 gpm) at pH 5.2 to 6.5 and metal concentrations of 34 mg/l Cr^{+6} and 34.7 mg/l Zn. The requirements for each of the chemicals needed for conventional treatment of this wastewater are:

Sodium bisulfite required--The theoretical requirement of $NaHSO_3$ for reduction of Cr^{+6} is 3 kg $NaHSO_3$ per kg Cr^{+6}*. Since an excess of about 50% over stoichiometric is normally required, the amount of $NaHSO_3$ needed is:

$$\frac{3.0 \text{ kg } NaHSO_3}{\text{kg } Cr^{+6}} \times 1.5 = \frac{4.5 \text{ kg } NaHSO_3}{\text{kg } Cr^{+6}}$$

Sulfuric acid required--To acidify the given wastewater from pH 5.5 to a resultant pH of 2.0 to 2.5, 516 mg/l of 66° Be' H_2SO_4 was required. On the basis of kg Cr^{+6} treated, this acid requirement would be:

$$\frac{1 \text{ l}}{34 \text{ mg } Cr^{+6}} \times \frac{10^6 \text{ mg}}{\text{kg}} = \frac{29{,}411 \text{l}}{\text{kg } Cr^{+6}} \times \frac{5.16 \times 10^{-4} \text{ kg}}{\text{l}} = \frac{15.18 \text{ kg } H_2SO_4}{\text{kg } Cr^{+6}}$$

The stoichiometric requirement of H_2SO_4 for reduction of Cr^{+6} is 1.49 kg H_2SO_4/kg Cr^{+6}*. Therefore, the total H_2SO_4 requirement for reduction of Cr^{+6} in this waste is:

$$\frac{15.18 \text{ kg } H_2SO_4}{\text{kg } Cr^{+6}} + \frac{1.49 \text{ kg } H_2SO_4}{\text{kg } Cr^{+6}} = \frac{16.7 \text{ kg } H_2SO_4}{\text{kg } Cr^{+6}}$$

Hydrated lime required--The amount of $Ca(OH)_2$ required to readjust the acidified waste from pH 2 up to a resultant value of 8.0-9.0 was 750 mg/l as $Ca(OH)_2$. Translating this concentration to the kg Cr^{+6} treated basis, the lime requirement is:

$$\frac{1\text{l}}{34 \text{ mg/l } Cr^{+6}} \times \frac{10^6 \text{ mg}}{\text{kg}} = \frac{29{,}411\text{l}}{\text{kg } Cr^{+6}} \times \frac{7.50 \times 10^{-4} \text{ kg}}{\text{l}} = \frac{22 \text{ kg } Ca(OH)_2}{\text{kg } Cr^{+6}}$$

Polyelectrolyte required--To flocculate metal hydroxide precipitates, anionic polyacrylamide polymers are frequently used at dosages of approximately 1 mg/l. The required polymer, on the basis of kg Cr^{+6} treated, is:

$$\frac{29{,}411 \text{ l}}{\text{kg } Cr^{+6}} \times \frac{1.0 \times 10^{-6} \text{ kg}}{\text{l}} = \frac{0.03 \text{ kg Polyelectrolyte}}{\text{kg } Cr^{+6}}$$

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*Ward, A. E., Wastewater Control and Treatment. In: Electroplating Engineering Handbook, 3rd Ed, A. K. Graham, ed. Van Nostrand Reinhold Company, New York, New York, 1971, pp. 360.

Cost of Chemicals Required--

The chemical cost, per kilogram of metal removed, for conventional treatment of the wastewater at Holley, is as follows:

$$\text{Sodium bisulfite} = \frac{4.5 \text{ kg } NaHSO_3}{\text{kg } Cr^{+6}} \times \frac{\$0.507}{\text{kg } NaHSO_3} = \frac{\$2.28}{\text{kg } Cr^{+6}}$$

$$\text{Sulfuric acid} = \frac{16.6 \text{ kg } H_2SO_4}{\text{kg } Cr^{+6}} \times \frac{\$0.103}{\text{kg } H_2SO_4} = \frac{\$1.71}{\text{kg } Cr^{+6}}$$

$$\text{Hydrated lime} = \frac{22 \text{ kg } Ca(OH)_2}{\text{kg } Cr^{+6}} \times \frac{\$0.103}{\text{kg } Ca(OH)_2} = \frac{\$2.27}{\text{kg } Cr^{+6}}$$

$$\text{Polyelectrolye} = \frac{0.03 \text{ kg polymer}}{\text{kg } Cr^{+6}} \times \frac{\$4.95}{\text{kg polymer}} = \frac{\$0.15}{\text{kg } Cr^{+6}}$$

$$\text{TOTAL CHEMICAL COST} = \frac{\$6.41}{\text{kg } Cr^{+6}}$$

Therefore, the estimated chemical cost of removing Cr^{+6} conventionally is \$6.41/kg Cr^{+6}.

The estimated lime dosage for conventional Zn removal, as $Zn(OH)_2$, is 1.22 kg $Ca(OH)_2$/kg Zn. The cost of lime plus polyelectrolyte for the removal of Zn is \$0.23/kg Zn. Combined removal of 1.61 kg/shift Cr^{+6} and 1.63 kg/shift Zn is, therefore, \$10.67/shift.

Costs for sludge handling in a conventional hydroxide treatment system can not be accurately estimated for purposes of comparison with "Sulfex"TN. In order to determine the cost of dewatering of the hydroxide sludge and the resultant volume to be disposed, parallel tests with the "Sulfex"TN system would have to be run. Such tests were beyond the scope of this demonstration.

CAPITAL AND INSTALLATION COSTS

Equipment Costs

Description	Estimated	Actual
Permutit Equipment	$ 92,465	$ 92,465
Engineering Costs	650	17,400
Includes:		
Consulting Engineering		
Report to State for Approval		
Design for Underground Tanks		
Underground Tanks†	16,000	48,000
Shipping and Installation	17,208	21,730
Taxes	1,164	1,089*
TOTAL CAPITAL COST	$117,487	$181,534

† Due to unfavorable ground conditions, the underground tanks could not be installed at this location. As a result, more expensive tanks had to be constructed above ground. These tanks include a new enclosure structure for protection of equipment and controls.

* Taxes on Permutit equipment only; all other taxes are included in other costs.

Expenses

Description	Estimated	Actual
System Evaluation (demonstration test)	$ 17,055	$ 17,055
Rearrangement of Existing Equipment	2,000	6,644
Laboratory Analyses	0	5,280*
	$ 19,055	$ 28,907

* These expenses are due to the EPA study of the wastewater treatment process. It involved analyzing four samples each day (two treated and two untreated) for 28 days. Normally, only one treated composite sample, on a weekly or monthly basis, is required.